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MICROGRAVITY MATERIALS SCIENCE CONFERENCE

Research Summaries

Huntsville, Alabama
May 24 & 25, 1994



*Organized
by*

Microgravity Materials Science Discipline Working Group

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Special Topics	Chair, Robert Schaefer	
Arnold Dahm		1
<i>Directional Solidification in ^3He-^4He Alloys</i>		
Lon J. Mathias		3
<i>Polymerizations in Microgravity</i>		
 Glasses & Ceramics I	 Chair, Peter Voorhees	
P. K. Dutta		5
<i>Reverse Micelle Based Synthesis of Microporous Materials In Microgravity</i>		
J. K. Richard Weber		7
<i>Containerless Liquid Phase Processing of Ceramic Materials</i>		
John J. Moore		9
<i>The Synergistic Effect of Ceramic Material Synthesis Using Vapor Enhanced Reactive Sintering Under Microgravity Conditions</i>		
 Glasses & Ceramics II	 Chair, Rohit Trivedi	
Dennis W. Readey		13
<i>Effects of Microgravity on Vapor Phase Sintering</i>		
Delbert E. Day		15
<i>Advanced Photonic Materials Produced by Containerless Processing</i>		
Irvin Glassman		17
<i>Combustion Synthesis of Materials in Microgravity</i>		
 Glasses & Ceramics III	 Chair, Dennis Readey	
Chandra S. Ray		19
<i>Kinetics of Phase Transformation in Glass Forming Systems</i>		
Kenneth F. Kelton		21
<i>Kinetics of Phase Transformations in Glass Forming Systems</i>		
Reid F. Cooper		23
<i>Glass Formation and Nucleation in Microgravity Containerless-Processed, Inviscid Silicate/Oxide Melts: Ground-Based Studies</i>		

Electronic Materials I	Chair, Richard Hopkins	
G. J. Abbaschian		25
<i>In-Situ Monitoring of Crystal Growth Using MEPHISTO</i>		
Ravindra B. Lal		27
<i>Solution Growth of Crystals in Low Gravity</i>		
Electronic Materials II	Chair, Tim Anderson	
Robert A. Brown		29
<i>Modelling of Convection and Crystal Growth in Directional Solidification of Semiconductor and Oxide Crystals</i>		
N. B. Singh		33
<i>Double Diffusive Convection During Growth of Lead Bromide Crystals in Space</i>		
Aleksandar G. Ostrogorsky		35
<i>Crystal Growth and Segregation Using the Submerged Heater Method</i>		
Electronic Materials III	Chair, Frank Szofran	
August F. Witt		37
<i>Identification of Gravity Related Effects on Crystal Growth, Segregation, and Defect Formation in BSO ($\text{Bi}_{12}\text{SiO}_{20}$)</i>		
Mohammad Kassemi		39
<i>Combined Heat Transfer Analysis of Crystal Growth</i>		
Electronic Materials IV	Chair, Tim Anderson	
Michael J. Kaufman		41
<i>Fundamentals of Thermomigration of Liquid Zones Through Solids</i>		
Daniel W. Mackowski		43
<i>Numerical Investigation of Thermal Creep and Thermal Stress Effects on Microgravity Physical Vapor Transport</i>		
Graham D. deVahl Davis		45
<i>The Effect of Gravity on Natural Convection and Crystal Growth</i>		

Electronic Materials V	Chair, Frank Szofran	
Sandor L. Lehoczky		47
<i>Growth of Solid Solution Single Crystals</i>		
Archibald L. Fripp		49
<i>Compound Semiconductor Growth in Low g Environment</i>		
David J. Larson		51
<i>Orbital Processing of High Quality Cadmium Telluride Compound Semiconductors</i>		
Sandor L. Lehoczky		53
<i>Crystal Growth of II-VI Semiconducting Alloys by Directional Solidification</i>		
Electronic Materials VI	Chair, Richard Hopkins	
David H. Matthiesen		55
<i>The Study of Dopant Segregation Behavior During the Growth of GaAs in Microgravity</i>		
Heribert Wiedemeier		57
<i>Vapor Transport Crystal Growth of Mercury-Cadmium-Telluride in Microgravity</i>		
Lodewijk van den Berg		59
<i>Vapor Crystal Growth of Mercuric Iodide</i>		
Electronic Materials VII	Chair, Robert Schaefer	
David H. Matthiesen		61
<i>Diffusion Processes in Molten Semiconductors</i>		
Allan S. Myerson		63
<i>Diffusion, Viscosity and Crystal Growth in Microgravity</i>		
Electronic Materials VIII	Chair, Tim Anderson	
Archibald L. Fripp		65
<i>Melt Stabilization of PbSnTe in a Magnetic Field</i>		
Frank R. Szofran		67
<i>Test of Magnetic Damping of Convective Flows in Microgravity</i>		
Electronic Materials IX	Chair, Richard Hopkins	
Ching-Hua Su		69
<i>Crystal Growth of ZnSe and Related Ternary Compound Semiconductors by Physical Vapor Transport</i>		
Ivan O. Clark		71
<i>Microgravity Chemical Vapor Deposition</i>		

Metals & Alloys I	Chair, Jon Dantzig	
Mary Helen McCay		73
<i>Casting and Solidification Technology (CAST)</i>		
William H. Hofmeister		75
<i>Containerless Processing of Oxide Superconductors</i>		
Metals & Alloys II	Chair, John Perepezko	
Barry Andrews		77
<i>Coupled Growth in Hypermonotectics</i>		
Merton C. Flemings		79
<i>Alloy Undercooling Experiments</i>		
L. A. Boatner		81
<i>Gravitational Effects on the Development of Weld-Pool and Solidification Microstructures</i>		
Metals & Alloys III	Chair, Peter Voorhees	
Richard N. Grugel		83
<i>Evaluation of Microstructural Development in Bulk, Undercooled Alloys</i>		
Thomas A. Lograsso		85
<i>Microstructural Development During Directional Solidification of Peritectic Alloys</i>		
Robert A. Brown		89
<i>Microstructure Formation During Directional Solidification of Binary Alloys: Experiment and Computation</i>		
Metals & Alloys IV	Chair, John Perepezko	
Christoph Beckermann		93
<i>Transport Phenomena During Equiaxed Solidification of Alloys</i>		
Kenneth A. Jackson		95
<i>Non-Equilibrium Phase Transformations</i>		
William L. Johnson		97
<i>Thermophysical Properties of Metallic Glasses and Undercooled Alloys</i>		

Metals & Alloys V	Chair, Jon Dantzig	
Ared Cezairliyan		99
<i>Optical Properties for High Temperature Materials Research</i>		
Robert H. Hauge		101
<i>Containerless Thermophysical and Thermochemical Property Measurements for Liquid Metals and Alloys</i>		
Julian Szekely		103
<i>Measurement of the Viscosity and Surface Tension of Undercooled Melts Under Microgravity Conditions and Supporting MHD Calculations</i>		
Shankar Krishnan		105
<i>Containerless Property Measurement of High Temperature Liquids</i>		
Metals & Alloys VI	Chair, Rohit Trivedi	
Robert J. Bayuzick		107
<i>Effects on Nucleation by Containerless Processing</i>		
John H. Perepezko		109
<i>Containerless Processing for Controlled Solidification Microstructures</i>		
Randall M. German		111
<i>The Gravitational Role in Liquid Phase Sintering</i>		
Peter W. Voorhees		113
<i>Coarsening in Solid-Liquid Mixtures</i>		
Metals & Alloys VII	Chair, Robert Schaefer	
R. Narayanan		117
<i>An Electrochemical Method to Measure Diffusivity in Liquid Metals</i>		
Frans A. Spaepen		121
<i>Crystal Nucleation, Hydrostatic Tension & Diffusion in Metal and Semiconductor Melts</i>		
Franz Rosenberger		123
<i>Temperature Dependence of Diffusivities in Liquid Metals</i>		
Metals & Alloys VIII	Chair, Dantzig/Trivedi	
David R. Poirier		125
<i>Comparison of the Structure and Segregation in Dendritic Alloys Solidified in Terrestrial and Low-Gravity Environments</i>		
Doru M. Stefanescu		127
<i>Particle Engulfment and Pushing by Solidifying Interfaces</i>		
Robert E. Apfel		129
<i>Foam Metallic Glass</i>		

SPECIAL TOPICS

Directional Solidification in ^3He - ^4He Alloys

Ming-Tang Chen and A.J. Dahm

Summary

The crystal growth phenomena in alloys which is under study here comes under the heading of directional solidification in alloys. Within a certain range of the speed of a moving liquid-solid interface interesting morphologies develop. These include periodic cellular patterns of the advancing solid separated by a thin region of solute of enhanced concentration pushed aside by the advancing fingers. Experimental studies of the transition from planar to cellular growth and the instabilities of the cells at higher growth speeds provide a basis to test theoretical models of the solidification of alloys. Such studies require visual observation and are limited to transparent alloys of which only a few have been studied. We study a different transparent alloy, a ^3He - ^4He mixture.

The properties of helium isotopic solutions differ considerable from those of the classical materials studied to date, and the parameters can be varied over a wide range. Solidification takes place by varying the pressure at constant temperature rather than by applying a temperature gradient at constant pressure. There are three particular advantages in using this alloy: (1) the width of our cell, ~ 1 mm, is less than the capillary length so that a two-dimensional sample can be studied. At the same time, planar surfaces can be formed over large areas so that investigations of three-dimensional samples can be studied in wider cells. (2) the effect of concentration gradients alone, as opposed to combined concentration and temperature gradients, can be studied at low ^3He concentrations in the superfluid phase of helium where the latent heat of fusion is nearly zero and the heat transport through the liquid is very efficient. (3) the melting curves in the P-T plane for different isotopic concentrations cross, i.e., the quantity dP/dc , the derivative of the melting pressure with concentration, varies from negative to positive. Regions of enhanced ^3He concentration melt at a lower or higher pressure than the average concentration depending on the temperature. Thus, studies can be made at temperatures where ^3He rich regions will remain in the liquid state, at temperatures where such regions will prefer to solidify, or at temperatures

(the crossings) where there is no preference. Studies of cellular formation in the regions where the melting curves for two different concentrations cross and a study of both two-dimensional and three-dimensional samples will provide data to tests theoretical models and enhance our knowledge of alloy solidification.

The goal of the proposed work is to enhance our fundamental understanding of crystal growth kinetics, liquid-solid interface morphologies and of the stability of alloys. A more complete understanding of the process of alloy crystallization and of desired and undesired interface morphologies which occur during solidification would enhance our ability to design alloys with specific material properties and to produce alloys of greater strength. The study of morphologies is of intrinsic interest in testing theories of non-linear systems. These studies will provide a base for future flight based research.

We have designed and built a cell capable of withstanding 30 atm pressure at a temperature of 1 K with an optical access of 0.75" by 1.5". A strong electric field at the tip of a tungsten needle located at the bottom of the cell provides an electrostrictive pressure and initiates the seed crystal. A single crystal is grown from this seed. We have studied the solid-liquid interface in pure ^4He and in concentrations of up to 100 ppm of ^3He at growth velocities up to several cm/sec. In these systems the interface remains in the horizontal plane with the solid phase occupying the lower half of the cell. At ^3He concentrations of 1%, crystal growth is initiated on the glass windows when the pressure is increased rapidly in an attempt to force a rapid advance of the solid-liquid interface. The preference for growth on the glass surface may result from a layer of ^3He forming at the solid-helium interface. Our cell has been redesigned, and a heat gradient will be imposed in an attempt to prevent solid growth on the viewing windows. We are ready to begin a systematic study of the interface morphology as a function of interface velocity, temperature and ^3He concentration between 100 ppm and 1%.

Polymerizations in Microgravity

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MSAD

Polymer Science

Polymer Science

Chemistry

University of Southern Mississippi

OBJECTIVES:

We are investigating the effects of gravity on three dynamic systems in which kinetics controls overall behavior as much as thermodynamics: free radical homo- and copolymerizations in dilute solution, traveling front polymerizations in bulk samples, and the behavior of polymeric emulsifiers and emulsions under flowing and static conditions.

DESCRIPTION:

Polymerization processes and polymer solution properties depend on the combined effect of kinetically determined behavior and thermodynamic properties. For example, diffusion of monomer to polymerizing chain ends competes with degradative termination to control molecular weight and polydispersity. While monomer diffusion is fast, polymer diffusion is slow. The rate of competing reactions can therefore depend on microscopic and macroscopic properties such as viscosity and mechanical mixing. We are attempting to develop experimental methods which will test the limits of these components on overall properties. We are examining a range of systems that will encompass the least likely to be effected (homo- and copolymerizations) up to those most clearly dependent on macroscopic forces. In the latter category is the behavior of polymeric emulsifiers for which shear-dependent behavior is modified by convective and density driven phase separation.

SIGNIFICANCE:

Understanding the individual contributing factors to the three main types of systems under study will allow more accurate prediction and control of behavior in earth-based applications. These studies all involve evaluation of the convective mixing effects (on earth) on solution, molten bulk and vapor phase polymer forming processes. In all three cases, gravity-driven complications limit our ability to observe and analyze individual rate constants and other reaction variables on the polymer formation and final properties. Ground-based research will help us understand the magnitude and type of interactions that can occur on a micro- and macroscopic level while microgravity studies will provide insight into the weaker interactions. Past work has shown large effects of gravity on the traveling front and polymer emulsifier systems, although a thorough understanding of how these effects are controlled by gravity is not available. Our long-range goal is to use the detailed knowledge available when the number of reaction variables are reduced (in microgravity) to understand and control similar processes on earth.

PROGRESS DURING FY 1994:

Our first year's efforts have involved achieving several synthetic targets and carrying out experimental design for the types of reaction and analysis hardware needed for both earth-based and microgravity experiments. The basic polymerization processes for the

solution and bulk systems to be studied have been defined and mapping of as many reaction variables as possible carried out. We have settled on simple homo- and copolymerizations plus cyclopolymerization and cyclocopolymerization for study of diffusion versus mixing controlled behavior in solution. We have determined relative rates of intra- versus intermolecular polyaddition for a series of dimeric acrylates, and have evaluated qualitatively the rates of propagation and chain transfer in ether and ester derivatives. This work lays the basis for copolymerization in which the relative rate of cyclization will be determined with respect to intermolecular propagation.

In the traveling front component, unexpected phenomena have been found. We have observed two instabilities in propagating fronts of methacrylic acid polymerization, both of which give the appearance of a spin mode. One occurs with liquid monomer when the tube is subjected to an external airflow to increase the rate of heat loss. It is a novel instability caused by convection related to bubble formation and may involve surface-tension driven convection. Spinning modes very similar to ones observed in solid-state combustion reactions were observed when the initial methacrylic acid/initiator solution was maintained at 0 °C. Both the helical pattern left in the polymer and temperature profile measured confirm for the first time the presence of a true spin mode in a constant velocity polymerization front.

Polymeric emulsifiers are a new class of compounds which offer significant advantages over conventional emulsifiers. For example, these compounds offer the feasibility of water-borne pesticides and herbicides with substantially reduced runoff in rainwater. The ultimate aim of this research is to design polymeric emulsifiers with optimal rheological properties for agricultural and pharmaceutical applications. The design pivots on a better understanding of the mechanism of emulsification.

Emulsions have been prepared under a range of different but well-defined shear rates. The results indicate that buoyancy is a significant factor in the final form of these emulsions. Differences in the specific gravity of the oil and water phases give rise to flocculation of oil droplets into large clusters, whereas isopycnic systems yield emulsions with single isolated droplets. Droplet size is reduced dramatically at a critical shear rate which is postulated to be the rate at which the polymer adopts a more open conformation.

PUBLICATIONS:

Basu, K.; Mathias, L. J. *Southeastern Graduate Polymer Conference*, April 13-15, 1994.

Thompson, R. D.; Barclay, T. B.; Basu, K. R.; Mathias, L. J. *Polymer Journal*, submitted.

J.A. Pojman, J. Willis, D. Fortenberry, V. Ilyashenko and A. Khan, submitted *J. Poly. Sci.*

Rulison, C.J.; Lochhead, R.Y.; Bui, H.S.; Pierce, T.D.; *Polym. Prprnts*, 34 (1), 863, 1993.

Lochhead, R.Y.; Rulison, C.J.; *Colloids and Surfaces*, accepted for December 1993.

GLASSES AND CERAMICS

Reverse Micelle Based Synthesis of Microporous Materials in Microgravity

PI - Prof. Prabir K. Dutta, The Ohio State University

Introduction

Microporous materials play an important role in chemical, petrochemical, environmental and consumer industries. The most extensively used materials in this class are the crystalline aluminosilicate zeolites, with typical compositions of $M_{2/x}O \cdot Al_2O_3 \cdot mSiO_2 \cdot nH_2O$. It should be noted that a large number of elements can be substituted for Si and for Al, thus creating an extensive array of materials. The most important characteristic of these compounds are the intrasolid channels and cages of molecular dimensions. Much of the interesting chemistry discovered with these materials occurs in the intracrystalline space. Thus, there is considerable effort worldwide in the synthesis of new frameworks with different topologies. It is recognized that such efforts would be considerably facilitated if our fundamental understanding of the complex crystal growth process is enhanced.

Biomineralization processes are widely observed in nature, whereby an organic/biological interface is used to localize and direct growth of inorganic materials. There is presently considerable interest in both understanding and exploiting biomineralization in order to generate new materials. Previous work in this area has used organic superstructures such as micelles. Langmuir Blodgett films and polymers to generate small metal and semiconductor particles and oriented inorganic structures.

Objective This research program involves an integrated approach exploiting reverse micelles as the vehicle for introducing reactants as well as the site for nucleation to form microporous materials. The goals of this research program are to grow microporous materials from reverse micelles, and to evaluate the mechanism of formation of microporous materials.

The experiments have been designed such that the continuation of the earth-based work to microgravity is essential in order to gain a complete realization of the goals of this study.

Experimental Strategy

Microporous materials are typically synthesized under hydrothermal conditions. Complex polymerization-depolymerization reactions occur in building up the framework from simpler species. The synthesis typically involves a nucleation period followed by rapid growth of crystals. It has been shown that water as well as cation-water complexes play an important role in developing the microporosity. Much remains to be understood about the crystal growth process at a molecular level.

Reverse micelles are micro-droplets of water that are solubilized in hydrocarbon solvents via detergents. These water droplets provide a potentially novel environment for microporous material synthesis for three reasons. First, the structure of water is different from bulk systems and provides a novel crystal growth medium. Second, the organic interface provides a novel nucleation site, as evident from biomineralization studies. Third, the simplicity of the system allows for ready measurement of particle size by light scattering that can be correlated with nucleation and crystal growth.

In order to establish the feasibility of this approach, our initial experiments have focused on the microporous zincophosphate system, which can be formed at room temperature. In principle, results with this system should be readily extended to other microporous systems and is the long-term goal of this program.

Experimental Progress and Microgravity Research Plans:

1) Ground Based Research

We have, for the first time, successfully nucleated and grew zincophosphate microporous materials using reverse micelles. Using AOT(12 bis(2-ethylhexyloxy-carbonyl)-1-ethane

sulfonate) as detergent, reverse micelles containing Zn^{2+} and phosphate ions were prepared in n-hexane. Upon mixing these micelles, a clear solution is obtained, which remains so for several hours to days (depending on the phosphate) followed by the appearance of a cloudy solution, which settles out as a precipitate. Light scattering studies show a gradual growth in particle size starting from 60-70 Å followed by a rapid increase at the point where the solution turns cloudy. Analysis of the solid product by diffraction shows the formation of the microporous sodalite framework along with other condensed (P61, hoepite) or amorphous phases, the products primarily being controlled by the molecular nature of the phosphate. Four distinct crystal growth pathways (controlled by phosphate species) are of interest:

(A) For really slow nucleation time (7 to 10 days), it appears that the sodalite crystals are growing epitaxially.

(B) Crystal growth of sodalite (epitaxially), as well as formation of amorphous particles (7 days), which settle under gravity and form the condensed P61 phase in the settled phase.

(C) Rapid (< 1 day) precipitation of amorphous zincophosphate in the micelle and nucleation and growth to form sodalite crystals prior to settling. There is aggregation of crystals after settling.

(D) Rapid precipitation (< 1 day) of amorphous zincophosphate with only partial conversion to sodalite prior to settling.

2) Extension to microgravity

In all earth-based experiments, zincophosphate particles (amorphous or crystalline) begin to settle out as soon as they reach particle sizes of $> 0.2 \mu\text{m}$. This has seriously hampered our attempts to analyze the crystallization process as well as evaluate the novel environment of the micellar medium in nucleating microporous structures. Microgravity will allow us to extend the synthesis process, without the complications of sedimentation. The specific effects of microgravity on the four pathways mentioned above will form our initial set of experiments. Under microgravity conditions,

Pathway A will confirm if microporous materials can indeed grow epitaxially, a topic of considerable discussion in the community. If epitaxial growth occurs, then it establishes the feasibility of growing mixed microporous materials, a feat that has been discussed but never actually realized on earth.

Pathway B in microgravity is expected to result in the formation of a different phase than P61, since settling is prevented. This will establish if microporous material synthesis can be directed differently, just by virtue of remaining suspended. This will have an important bearing on the choice of future experiments with other microporous materials, where nucleation is typically slow.

Pathway D will also provide similar information. In microgravity, the important observation will deal with whether the amorphous suspended particles will transform to a crystalline material.

Pathway C under microgravity conditions will lead to formation of well-defined larger sodalite crystals as compared to earth based conditions.

The ground-based program has (a) established the validity of using reverse micelles as reactants as well as nucleation sites for microporous materials and thereby, the usefulness of biomineralization methods to form complex crystalline solids, and

(b) provided insight into the growth of microporous crystals, based on light scattering and morphology studies. Coupling these experiments with ^{31}P NMR will provide information on the molecular intermediates.

The microgravity experiments will (a) confirm the nature of epitaxial growth, thus leading to the possibility of synthesis of a new class of materials; (b) allow for growth of crystalline phases from suspended particles that contain the nutrients, but need longer times for nucleation, which is essential for growth of slower nucleating microporous materials; and (c) allow for the growth of large crystals, a technologically useful goal.

PROJECT SUMMARY

PROJECT TITLE: Containerless Liquid-Phase Processing of Ceramic Materials

April 27, 1994

Principal Investigator: Richard Weber, Containerless Research, Inc., Evanston, IL 60201, 708/467-2678

Co-Investigator: Paul C. Nordine, Containerless Research, Inc., Evanston, IL 60201, 708/467-2678

1. Project Objectives - Containerless methods provide a powerful tool for materials research at high temperatures. This research exploits the control of chemistry and nucleation achieved by containerless liquid-phase processing to study non-equilibrium phase formation and crystal growth in ceramic systems. The work has two primary objectives: (i) to probe the limits of ground-based containerless liquid-phase processing by working with high melting oxide- and boride-based ceramic and glass materials, and (ii) to conduct experiments on candidate systems for low gravity investigations. In addition, the investigators are collaborating with other NASA-supported researchers in containerless liquid-phase processing experiments using unique facilities for ground-based research that we have developed.

2. Relevance to Microgravity Research - The results obtained in ground-based investigations have advanced the understanding of the high temperature chemistry of refractory oxide and boride materials. Subsequent low gravity containerless experiments will provide the high degree of control over melts needed for measurement of the melt properties, for melt processing, and for investigation of solid-liquid phase relationships in well characterized thermodynamic states.

3. Background - Containerless methods enable unique high temperature process science investigations. A high degree of thermodynamic control over molten materials can be achieved in ground-based experiments by eliminating container-derived contamination and nucleation. Reduced gravity experimentation offers the possibility of controlling convective mass and heat transport, and segregation/sedimentation in melts - this "kinetic control" extends the range of experimental conditions allowing investigation of solidification and crystal growth, and providing conditions for measurements of fluid transport properties which influence solidification processes.

The work described here applied ground-based containerless processing to work with non-metallic materials. It addresses ways in which low gravity could extend the range of experimental conditions to provide fundamental and applied insights into process-structure-property relationships. Some of the work outlined in this summary is published or in the process of publication. Selected citations are listed at the end of this report.

4. Experimental Methods - High temperature liquid-phase processing was achieved by aero-acoustic or aerodynamic levitation in combination with continuous-wave CO₂ laser beam heating. Materials investigated were aluminum oxide, calcia-gallia and aluminum oxide-silicon dioxide based binary systems, YBaCuO ceramic superconductors, and rare-earth borides. Additional materials were investigated in collaboration with other NASA-supported scientists.

The effects of ambient oxygen pressure on the solidification behavior and properties of oxide-based melts was investigated by equilibrating the melts with controlled oxygen fugacity atmospheres. Selected specimens were characterized by optical microscopy, scanning electron microscopy, X-ray diffraction analysis, Raman spectroscopy, laser fluorescence, and solid state NMR spectroscopy.

5. Experimental Results - Key results are listed below.

(i) Aluminum oxide: structure and properties of the materials formed by containerless melting and solidification were shown to depend on the ambient oxygen pressure such that the material contained more

defects and was of a greater purity when processed at high oxygen fugacity.

(ii) YBaCuO: The solubility of yttrium oxide was shown to depend on the ambient oxygen pressure such that material processed under high purity argon allowed complete dissolution of Y_2O_3 in a few seconds, enabling deep undercooling to be achieved.

(iii) Calcia-Gallia materials: a factor of 6 reduction from 550 to 90 K/s in critical cooling rate to form glasses was demonstrated compared to material processed as a pendant drop in contact with a platinum-rhodium thermocouple.

(iv) Borides: Work to achieve melting of boride materials and eliminate the formation of borate slags was progressed using aerodynamic levitation in high purity argon.

(v) Cr^{3+} Fluorescence Measurements: Trace impurity removal was investigated by Raman spectroscopy and Cr^{3+} fluorescence in aluminum oxide and synthetic ruby specimens. The work is being conducted in collaboration with Dr. Abi Biswas at JPL. The Cr^{3+} fluorescence yield decreased exponentially with processing time. The rate of chromium loss was proportional to the concentration of dissolved chromium, and increased with the ambient oxygen pressure.

(vi) Solid-state NMR Spectroscopy - NMR spectra of processed materials were obtained by Drs. Coutures and Poe at the CNRS facility in Orleans, France. Lattice relaxation rates were unusually small in oxygen and even smaller in argon. These results indicate that the processed materials are of high purity and stoichiometry, more so in argon than in oxygen. The NMR investigations are continuing.

(v) Collaborative experiments to process materials provided by other NASA investigators were conducted with NASA-supported research groups from University of Missouri-Rolla, University of Wisconsin-Madison, and Vanderbilt University.

6. Current and Future Research - The main focus of the continuation will be to achieve complete, containerless melting of selected rare-earth boride phases and characterize the processed materials. The in-progress studies of the effects of ambient oxygen fugacity on structure-property relationships in melts will be continued. An objective is to couple thermophysical property measurements with NMR measurements to determine the changes which take place in liquids during processing and define the requirements for low gravity experiments. Collaborative research will be continued.

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3. J.R. Olive, W.H. Hofmeister, R.J. Bayuzick, G. Carro, J.P. McHugh, R.H. Hopkins, M. Vlasse, J.K.R. Weber, P.C. Nordine and M. McElfresh, J. Mat. Res., **9**, 1-3 (1994).
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5. J.K.R. Weber, C.D. Anderson, S. Krishnan and P.C. Nordine, "Structure of Aluminum Oxide Formed from Undercooled Melts," J. Am. Ceram. Soc., (in press).
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The Synergistic Effects of Ceramic Material Synthesis Using Vapor Enhanced Reactive Sintering Under Microgravity Conditions

NASA Contract NCC 3-289

January 1, 1993 - December 31, 1995

Principal Investigators:

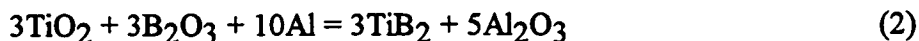
Dr. John J. Moore

Dr. Dennis W. Readey

Summary

Reaction Systems

The objective of this research is to determine the effects of convection of vapor species produced at the reaction front on the in situ formation of ceramic composites by high temperature exothermic synthesis reactions (combustion synthesis). In these systems the reaction is self-sustaining, once it has been initiated, on account of the reaction's own exothermicity. Two model exothermic reactions are used in the study:



Reaction (1) does not generate gaseous species from within the reaction itself. However, two quite different gaseous environments are used, i.e. an inert gas - argon, and a reactive gas - HCl gas. A fundamental research program has been initiated with the objective of obtaining a more complete understanding of the effects and interactions between reaction parameters (green density, dilution, mass, particle size, atmosphere pressure, and reaction pellet orientation with respect to gravity), vapor transport, and gravity on the combustion synthesis of titanium diboride (TiB_2) via reaction (1). The production of high quality submicron ceramic precursors may be accomplished efficiently and economically by this method.

Reduced gravity processing has proven to produce more homogenous ceramic materials in some systems than processing in normal (1g) conditions.¹ Production of ceramics with a fine grain size and narrow particle size distribution may be accomplished by conducting combustion synthesis reactions in a microgravity environment. The microgravity environment will eliminate convection currents, which can cause microstructural inhomogeneities, present in combustion synthesis reactions conducted in normal (1g) conditions. Thermal gradients, which can affect the cooling rates of the product, may also be changed.

To date, research on the effects of vapor transport and of reaction parameters on the combustion synthesis reaction in normal (1g) conditions has been completed for reaction (1).

Reaction system (2) generates at least one gaseous phase, i.e. B_2O_3 gas (boiling point $1860^{\circ}C$), at the reaction front since the combustion temperature of the reaction can be controlled between $1700^{\circ}C$ and $2200^{\circ}C$. At the same time, two liquids, i.e. Al (melting point $660^{\circ}C$), and B_2O_3 (melting point $450^{\circ}C$), are also created prior to initiation of the exothermic reaction (ignition temperature $950-1100^{\circ}C$). Hence, the effect of gravity on the convection of gaseous species generated at the reaction front and those deliberately provided from the atmosphere will be investigated, together with the effect of gravity-driven fluid flow, i.e. liquid Al and B_2O_3 , as a means of controlling the exothermic reaction. The main objective will be to provide a clear understanding of how the microstructure and properties of these low cost, rapid synthesis reaction products can be used to produce ceramic powders and composites.

Experimental Results to Date

Reactant powders are pressed into a compact and heated with a tungsten coil to induce the exothermic reaction. The reaction proceeds in the form of a propagating combustion wave and is completed in a matter of seconds, with the formation of a typically 50% porous product. However, the product microstructure has been shown to vary substantially as a function of reaction parameters and also within a single pellet.

Ground-based experiments with different environmental pressures and/or orientations with respect to gravity and the direction of propagation confirm that convection processes do indeed play an important role. Convection changes the product

microstructure both by modifying the heat distribution within the pellet and by changing the reaction stoichiometry due to the gaseous phases present. Analysis of the reactions has been conducted with video recordings of the propagating combustion reaction, x-ray diffraction, and scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) of the products. The grain size may be controlled, within limits, through control of the reaction parameters. Under microgravity conditions, convection effects can be minimized, since convection is a gravity-dependent process. Without convection, a more uniform and controlled product microstructure with respect to pore distribution and product morphology should be produced.

To date, the effects of both inert (Ar) and reactive gas (HCl) pressure, green density, dilution, reactant mass, particle size, and pellet orientation on ignition and combustion temperatures and product microstructure have been investigated. Future tests involve microgravity experiments aboard the NASA-Lewis Learjet which are currently scheduled to be conducted in May, 1994.

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THE EFFECT OF MICROGRAVITY ON VAPOR PHASE SINTERING

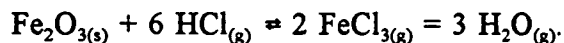
Principal Investigator: Dennis W. Readey
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STATEMENT OF THE PROBLEM

Vapor transport during sintering of ceramics can have a profound effect on microstructure. It can decrease the rate of densification by reducing surface curvature. At the same time, it can greatly enhance grain growth at all porosities further decreasing the rate of densification. On the other hand, vapor transport can be advantageously used to produce ceramics of controlled porosity and pore sizes which have potential for a number of applications, including filters. Some systems fit the existing particle growth models well and others do not. The reason for this is thought to be the competition between normal grain boundary motion and transport via the vapor phase. Microgravity offers the potential for experiments of relatively dispersed, unconstrained particles for which boundary motion will not play a role. Low temperature, non-toxic, high vapor pressure surrogate materials are being sought for microgravity experiments.

PREVIOUS RESULTS

Systematic investigations on the effect of vapor transport on microstructure development in ceramics have been carried out on CdO, SnO₂¹, and ZnO in hydrogen²; Fe₂O₃³, TiO₂⁴, ZrO₂⁵, Al₂O₃⁶ and ZrTiO₄, BaTiO₃, SrTiO₃, and PbTiO₃⁷ in HCl; and Si in H₂O-H₂ mixtures.⁸ The result is that the main effect of enhanced vapor transport on sintering is significant particle coarsening with virtually no densification. The results of Fe₂O₃ in HCl illustrate the point. In HCl, the following reaction dominates the transport species in the gas phase:



The particles grow with very close to a $t^{1/3}$ dependence and the particle size is within a factor of two of that calculated from coarsening models.^{9,10,11} However, Al₂O₃, which reacts in a similar fashion in HCl, shows very different results and does not fit the model well at all.⁶ The reason that Al₂O₃ is thought to not fit the model is that coarsening is inhibited by the constraints put on a particle in powder compact by its nearest neighbor particles.

MICROGRAVITY RATIONALE

The potential for microgravity in these studies is to provide an environment where particle coarsening can take place under relatively dispersed conditions and compare the results of coarsening of dispersed particles with those in a powder compact. The times for previous coarsening experiments have been as long as hundreds of hours. This implies that shuttle flights will be necessary. As a result, it is desirable to eliminate toxic or explosive

atmospheres such as HCl and hydrogen. Furthermore, low temperatures are much more amenable to microgravity experiments. Therefore, low temperature surrogates are being sought to investigate the same phenomena that are important at high temperatures in toxic atmospheres in ceramics. The desirable characteristics of low temperature surrogates are:

- high vapor pressure
- low melting point
- simple crystal structure
- non-toxic
- stable in air
- small particle size ($< 10 \mu m$)
- shows particle growth and no densification

Inorganic Surrogates

A list of some 50 potential inorganic compounds was compiled from the literature based on their melting points and vapor pressures. The following systems were chosen for further experimental investigation based primarily on their vapor pressures, melting points, and relative lack of toxicity: iron Chloride, $FeCl_3$; aluminum Chloride, $AlCl_3$; iodine, I_2 ; ammonium bromide and ammonium chloride, NH_4Br , and NH_4Cl ; and sodium chloride, $NaCl$. Preliminary experiments on particle growth with NH_4Cl and $NaCl$ have shown that these materials may exhibit the necessary coarsening phenomenon.

Organic Surrogates

Over thirty organic compounds were found in the literature that had high vapor pressures at low temperatures. Many were eliminated because of their alleged toxicity and others simply because their melting points were too low or their vapor pressures too high. An example of one such material is H_2O , ice. Two systems were chosen for further study: salicylic acid, $C_7H_6O_3$ and trans-cinnamic acid, $C_9H_8O_2$. Both of these materials could be successfully ball milled to produce small particle size material for initial screening experiments. However, the very high vapor pressures of these materials has precluded their investigation by SEM.

CONCLUSIONS

The necessity for long flights and non-toxic atmospheres has led to search for suitable low temperature surrogates to study vapor phase sintering of ceramics. There are several inorganic and organic compounds that appear promising. The very high vapor pressures at low temperatures for some of these compounds preclude the use of standard electron microscopy for analyzing the particle growth, either dispersed or in powder compacts.

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Summary Statement
(25 April 1994)

**ADVANCED PHOTONIC MATERIALS PRODUCED BY
CONTAINERLESS PROCESSING**
NASA Contract: NAGW-2846

Principal Investigator: Delbert E. Day, Curators' Professor of Ceramic Engineering and Senior Investigator, Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, MO 65401. Phone: (314)341-4354.
(Co-Investigator: Chandra S. Ray)

Contract Period: December 1991 to November 1994.

Task Objectives:

The objectives of this research were to 1) use containerless melting to investigate non-linear optical glasses which have the potential for use as ultra-fast, all optical switches and other photonic devices for communication and advanced computer application, and 2) investigate and compare the kinetics of nucleation and crystallization for these glasses prepared by containerless melting with the kinetics for the same glasses conventionally melted in a container.

Benefit or Necessity of Microgravity:

Glasses considered to possess the potential for non-linear optical applications such as the heavy metal oxide (HMO) glasses containing PbO , Bi_2O_3 , and Ga_2O_3 are, in general, highly fluid and chemically corrosive. These melts readily crystallize during cooling and develop unwanted color centers primarily due to impurities dissolved from the container. The traditional procedures used to melt these glasses generally yield colored and chemically inhomogeneous glasses of limited usefulness for non-linear optical applications.

Containerless melting, which can be achieved in low gravity, provides the opportunity to suppress or eliminate the undesirable heterogeneous nucleation and crystallization in such melts. Since no container is used, color centers caused by impurities dissolved from a container can be completely eliminated, even in highly corrosive melts. Containerless processing offers a viable alternative for preparing glasses with improved purity and homogeneity, and non-linear optical properties.

Results to-Date:

Among all the oxide glasses investigated to-date, the HMO glasses containing PbO , Bi_2O_3 , and Ga_2O_3 are reported to have the best non-linear optical properties. However, the orange to yellow color of these glasses is a potential disadvantage for their use in many applications, especially in optical devices. The initial task of the present work, therefore, was to investigate the elimination of color from glasses in this $\text{PbO-Bi}_2\text{O}_3\text{-Ga}_2\text{O}_3$ system. First, the melting parameters which generally affect the color of such HMO glasses such as the crucible material, melting temperature, time and atmosphere, and the starting raw materials were changed in an attempt to obtain colorless glasses. No conditions were found which totally eliminated the color. The range of compositions investigated was $x\text{PbO} \cdot (100-(x+y))\text{BiO}_{1.5} \cdot y\text{GaO}_{1.5}$ where x varied from 20 to 60 cat% and y equalled 20, 25, 30, or 35 cat%. The least, pale yellow, color was obtained for a $40\text{PbO} \cdot 35\text{BiO}_{1.5} \cdot 25\text{GaO}_{1.5}$ cat% glass (HMO-7) when it was melted in air or in

a nitrogen atmosphere in an alumina or gold crucible at 900°C for 30 min. The HMO-7 composition was then melted using two different containerless melting techniques developed at UMR. Glass beads 60 to 200 μm in diameter were easily obtained. These glass beads prepared by containerless melting, however, also had a pale yellow color. This result suggests that the typical yellow color is intrinsic to these glasses.

Because of the potential applications for these $\text{PbO-BiO}_{1.5}\text{-GaO}_{1.5}$ glasses, knowledge of their various properties is of considerable value. Properties such as the density, molar volume, thermal expansion coefficient, chemical durability, glass transition and crystallization temperatures, and transmission in the ultraviolet-visible and IR have been measured as a function of composition. The compositional dependence of these properties was consistent with the weight, size, charge, and bond strength of the cations. The glass forming tendency for these glasses increased with increasing $\text{GaO}_{1.5}$ and decreased with increasing PbO or $\text{BiO}_{1.5}$ content. The Ga^{3+} ions in these glasses are believed to act primarily as network-forming cations, whereas, the majority of the Bi^{3+} and Pb^{2+} ions behave as network-modifying cations. A small fraction of the lead ions are probably present as Pb^{4+} .

Present and Future Work:

Very little is known about the structure of the $\text{PbO-Bi}_2\text{O}_3\text{-Ga}_2\text{O}_3$ glasses. A collaborative research program between the University of Missouri-Rolla (UMR) and the Jet Propulsion Laboratory (JPL) is underway to investigate the structure of these glasses using high temperature XRD (x-ray diffraction analysis), IR and Raman Spectra. The IR and XRD, as a function of glass composition and temperature, are now being measured at UMR while the Raman spectra are being measured at JPL.

Since the color of the $\text{PbO-Bi}_2\text{O}_3\text{-Ga}_2\text{O}_3$ glasses could not be eliminated even by containerless melting, our attention has shifted to other heavy metal glasses which have potential use in non-linear optical applications. Nearly colorless glasses in the PbO-TeO_2 system have already been prepared and a few selected properties such as the third order non-linear susceptibility are now being measured.

Publication/Presentation:

This research has been described at the 1993 annual meeting of the American Ceramic Society and in three technical publications (see extended report for references). A fourth paper is being prepared in collaboration with JPL.

Collaboration:

This NASA-sponsored research has also led to collaboration with several national and international organizations such as Intersonics Incorporated (Illinois), JPL, Washington University in St. Louis (Missouri), and Osaka National Research Institute (ONRI) in Japan. The research program with JPL has been described above. Intersonics and UMR have been measuring the critical cooling rate for containerless melts using an aero/acoustic levitator furnace. The kinetics of nucleation and crystallization in several glasses are being investigated in collaboration with Washington University through computer simulation and experimental DTA/DSC measurements. Four experiments consisting of melting, evaporating and resolidifying tellurite glasses in Japan's new 710m drop shaft have been completed in collaboration with ONRI, Japan.

COMBUSTION SYNTHESIS OF MATERIALS IN MICROGRAVITY

Grant NAG3-1418

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INTRODUCTION

A comprehensive experimental and theoretical program has begun in order to synthesize metallic and nonmetallic nitrides, especially titanium nitride, under microgravity conditions and, in doing so, to understand the underlying combustion mechanisms. The experimental program applies the Self-Propagating High-Temperature Synthesis (SHS) technique to titanium (or other metal) particle suspensions in liquid and supercritical nitrogen. In principle, the nitride particles are formed in these fluids upon passage of a self-sustained flame through the suspension. As will be described shortly, experiments already conducted with liquid nitrogen/powdered titanium slurries confirm that titanium nitride can be formed in this manner.

Microgravity conditions, when invoked, will prevent particle settling, agglomeration and liquid metal film formation. Microgravity conditions should also permit the use of suspensions and particles of specified characteristics, and facilitate the production of nitride powders of high purity, uniformity and specificity. The novel use of supercritical nitrogen, an extension of current experiments with liquid nitrogen, will provide an abundant supply of reactant which at conditions near the critical temperature and pressure, not only avoids the bubble formation that occurs with liquid nitrogen, but also provides a means for greatly changing reactant density through a modest change in pressure.

The theoretical investigation which involves analyses of the propagation, structure, and stability of the heterogeneous diffusion flame, and the reaction mechanisms of individual metal particles in variable density fluids builds on previous theoretical developments at Princeton.

EXPERIMENTAL

a) Titanium Compacts

After conducting a number of preliminary experiments duplicating results reported in the literature for the reaction of compacted titanium powder with gaseous nitrogen, a series of experiments were conducted with liquid nitrogen. In the initial set of experiments, the titanium powder (average diameter is 20 microns) was pressed in a die to form a cylindrical compact varying in density from 54 to 65 % of the maximum possible. The titanium compact was ignited from the bottom by a wound tungsten filament with a diameter comparable to that of the compact.

Examination of the cylindrical compacts after the combustion process had completely self extinguished indicated, in general for four experiments, the following characteristics. There was a thin titanium shell, approximately 1-2 mm deep, around the circumference of the compact. Just inside this shell extending inward for another 1-2mm was a yellow brown/purple colored shell that was confirmed by Wavelength Dispersive Spectroscopy to be titanium nitride or a solution of nitrogen in titanium. .

Interior to this shell was gray metallic material that was titanium and titanium - nitride solution. Along stress fractures within this gray center there was yellow brown material indicating that titanium nitride had formed. From these observations it can be concluded that the pressed powders did not have sufficient accessible nitrogen to lead to complete conversion. Only near the surface or through stress created channels could the nitrogen be supplied sufficiently fast, compared to heat loss to the liquid nitrogen, for the formation of the nitride.

b) Titanium/Liquid Nitrogen Slurries

Accessibility of nitrogen to the reacting titanium particles would be facilitated by looser packing of the titanium powders to form the cylindrical shape. However, loosely packed compacts with less than 50% theoretical density could not maintain their structural integrity in the liquid nitrogen sufficiently long to conduct the combustion experiment. Instead of very loosely packed compacts, low density slurries or suspensions of titanium powder reacting in liquid and supercritical nitrogen have been suggested in our NASA proposal as a means of providing the necessary nitrogen to the reacting titanium particle. A series of experiments with dense slurries of titanium powder in liquid nitrogen was begun in order to develop the techniques and experience necessary to form low density slurries of scientific interest.

To supply nitrogen continuously to the reacting titanium an unsealed tube was fitted with a porous stainless steel wire mesh at one end. The igniter filament was placed approximately midway along the height of the tube so that a titanium powder slurry would fill in the space below and above the filament. After the titanium powder was placed in the tube, the upper end was also fitted with a porous mesh. The whole assembly was then placed in a liquid nitrogen containing Dewar flask.

After ignition, two flames were observed to propagate outward from the tungsten igniter, one upward and the other downward. The downward flame reached the bottom stainless steel mesh and burned through it. However, the titanium powder above the bottom mesh had been converted by the combustion wave to a solid titanium nitride column and thus remained in the tube. The titanium nitride column throughout had the golden brown color of titanium nitride with some occasional spots of gray metallic material presumably from the melting of unreacted titanium. The titanium nitride column was highly porous which indicated that nitrogen had been accessible to almost all the titanium powder. The high accessibility of nitrogen appeared to be responsible for the almost complete conversion of the titanium to titanium nitride.

THEORY

Theoretical work has been conducted through a fruitful collaboration between Professor Law of Princeton and Professor A. Makino of Shizuoka University in Japan. The work has already led to two refereed publications:

"On the SHS Combustion Characteristics of Several Ceramics and Intermetallic Compounds", J. Am. Ceramic Soc. (1993), in press.

"Propagation and Diffusion Limited Extinction of Nonadiabatic Heterogeneous Flames in the SHS Process", Twenty-Fifth Symposium on Combustion (1994), accepted for publication.

The theoretical work has focused on developing the fundamental understanding necessary for the interpretation of the solid-gas combustion synthesis process by first addressing the conceptually simpler solid-solid system.

Summary Statement
(25 April 1994)

KINETICS OF PHASE TRANSFORMATION IN GLASS FORMING SYSTEMS
NASA Contract: NAG8-898

Principal Investigator: Chandra S. Ray, Research Professor, Department of Ceramic Engineering and Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, MO 65401. Phone: (314)341-6432
Contract Period: 15 November 1991 to 14 November 1994.

Task Objectives:

The objectives of this research were to (1) develop computer models for realistic simulations of nucleation and crystal growth in glasses, which would also have the flexibility to accommodate the different variables related to sample characteristics and experimental conditions, and (2) design and perform nucleation and crystallization experiments using calorimetric measurements, such as differential scanning calorimetry (DSC) and differential thermal analysis (DTA) to verify these models.

The variables related to sample characteristics mentioned in (1) above include size of the glass particles, nucleating agents, and the relative concentration of the surface and internal nuclei. A change in any of these variables changes the mode of the transformation (crystallization) kinetics. A variation in experimental conditions includes isothermal and nonisothermal DSC/DTA measurements. Isothermal kinetic studies yield reasonably accurate information about the mode of transformation and the activation energies of nucleation and growth, but nonisothermal measurements have several advantages. The nonisothermal measurements are easier to perform and less time consuming, and they can probe the kinetics of transformation over a different, generally higher, temperature range than is possible from isothermal methods. However, the thermoanalytical models presently used to analyze the nonisothermal kinetic data are considered to be fundamentally flawed, since they are based on erroneous assumptions for the temperature dependence of the effective rate constants, generally, resulting in misinformation about the transformation processes. This research would lead to develop improved, more realistic methods for analysis of the DSC/DTA peak profiles to determine the kinetic parameters for nucleation and crystal growth as well as to assess the relative merits and demerits of the thermoanalytical models presently used to study the phase transformation in glasses.

The present research is a part of a collaborative research program supported by NASA through two separate contracts. The experimental work is conducted at the University of Missouri-Rolla (NASA Contract NAG8-898, PI: C. S. Ray) and the theoretical work is conducted at the Washington University in St. Louis (NASA Contract NAG8-873, PI: K. F. Kelton).

Benefit or Necessity of Microgravity:

Existing experimental evidences on solidification of glass forming melts in microgravity point to the importance of investigating the kinetics of nucleation and crystallization in a more generalized and realistic way. For example, glasses prepared in microgravity are reported to be more chemically homogeneous and more resistant to crystallization than identical glasses

prepared on earth. These results indicate that the size, number density, and distribution of nuclei, and, hence, the nucleation mechanism, are different in glasses prepared in space and on earth. To verify these apparently surprising observations, realistic thermoanalytical models as well as experimental data on phase transformation in glasses prepared in space are needed.

Results to-Date:

The results obtained for the theoretical part of this work have been reported separately by Dr. K. F. Kelton of the Washington University in St. Louis (NASA Contract: NAG8-873). The devitrification of silicate based glasses that transform to a crystal of the same composition by homogeneous nucleation is investigated. A lithium-disilicate, $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (LS_2) and a soda-lime-silica, $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ (NC_2S_3) glass are used for most experimental measurements, since the necessary kinetic and thermodynamic parameters are available for these glasses. Significant accomplishments achieved to-date are summarized below.

1. Using a DTA technique previously developed for a LS_2 glass, nucleation rate-temperature like curves for undoped and doped NC_2S_3 glasses were determined. The dopants used in the NC_2S_3 glass were small amounts of platinum, Ag_2O , and P_2O_5 . The temperature range for nucleation and the temperature for maximum nucleation determined from these curves, which were obtained by plotting $1/T_p$ (T_p is the temperature at the DTA peak maximum) or $(\delta T)_p$ ($(\delta)_p$ is the DTA peak height at T_p) against the nucleation temperature, T_n , were in excellent agreement with those determined by other, more time consuming methods. It appeared that the shape of the $(\delta T)_p$ vs. T_n plots for these glasses depended upon whether the nucleation rate (I) and growth rate (U) curves overlapped, while that of the $1/T_p$ vs. T_n plots were independent of the overlap of I and U.
2. A theoretical model was developed and used to explain the shape dependence of the $(\delta T)_p$ vs. T_n curves upon the overlap of I and U. In this model it was assumed that $(\delta T)_p$ was linearly proportional to the total number of nuclei present in the glass sample under investigation, which was experimentally demonstrated to be correct for a LS_2 glass.
3. Similar nucleation rate-temperature like curves were also determined for a LS_2 glass from dielectric constant and $\tan \delta$ (loss) measurements using samples isothermally nucleated at different temperatures for 3 h and crystallized at 660°C for 15 min.
4. The effect of DTA heating rate on nucleation was investigated using the LS_2 glass. It was demonstrated that for heating rates less than $3^\circ\text{C}/\text{min}$, a significant number of new nuclei formed during the DTA scan, which increases with decreasing heating rate. No new nuclei was found to form in this LS_2 glass for heating rates $> 3^\circ\text{C}/\text{min}$.

Present and Future Work:

- (1) Effect of DTA scan rate on nucleation for the NC_2S_3 glass.
- (2) Dependence of DTA peak height and peak temperature on particle size of the LS_2 glass with and without nucleating agent.
- (3) Estimation of nucleation rate, I, at different temperatures from $(\delta T)_p$ vs. T_n plot for the LS_2 glass.
- (4) Study the usefulness of a recently developed technique for determining the nucleation rate-temperature like curves from dielectric constant measurements using other glasses, such as $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{BaO} \cdot 2\text{SiO}_2$.

Presentation/Publication:

This research has lead to six presentations and two publications, the detailed references of which are given in the extended report.

Kinetics of Phase Transformation in Glass Forming Systems

Summary of the research performed under NAG 8-873

Professor Kenneth F. Kelton
Washington University
St. Louis, MO 63130

Background: Existing experimental evidence on phase formation and stability in a microgravity environment points to the importance of containerless solidification and the control of convection in obtaining desired phases and microstructures. Most information is gained from microstructural studies on samples treated under different experimental conditions. Little direct data on the effect of microgravity on the kinetics of phase transformation is available, however.

Precision calorimetric measurements, such as differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are most commonly used to study the kinetics of phase transitions in the laboratory. When coupled with detailed microscopic studies of the transformation microstructure, isothermal kinetic studies can yield information about the mode of transformation and the activation energies of nucleation and growth. Nonisothermal kinetic measurements have several advantages over isothermal measurements. The measurements are easier to make and less time consuming, they require less sample, and they can probe the kinetics of transformation over a different, generally higher, temperature range than is possible from isothermal methods. Automation of nonisothermal data collection should be possible, allowing such measurements to be easily made at remote locations, such as in a microgravity environment. Nonisothermal methods, however, suffer from the lack of quantitative methods for analysis. Existing methods are based on erroneous assumptions for the temperature dependence of the effective rate constants, generally resulting in misinformation about the transformations.

Objectives and Research Description: The objectives of this research are to develop computer models for realistic simulations of first order phase transformations, and to design experiments to test those models. The devitrification of silicate based glasses that transform polymorphically to a crystal of the same composition by homogeneous nucleation is studied. Lithium disilicate ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$) is used for most calculations and experimental measurements, since the necessary kinetic and thermodynamic parameters are well known. Soda-lime-silicate glasses ($\text{Na}_2\text{O} \cdot 0.2\text{CaO} \cdot 3\text{SiO}_2$) are also being studied as are the effects of nucleating agents on the transformation. This work is carried out in collaboration with Drs. C. Ray and D. Day of the University of Missouri, Rolla, under a related contract; they prepare the glasses and make DTA studies of their crystallization. The computer modeling is carried out in my group at Washington University. Scanning (SEM) and transmission (TEM) electron microscopy and DSC studies are also made in my group.

As already mentioned, this research will lead to improved methods for the analysis of

phase transformation kinetic data, allowing, for example, kinetic parameters for nucleation and growth to be determined from peak profiles obtained by DSC. Our computer models are also being used to evaluate existing methods of analysis, showing in what regimes they might be valid. The new techniques developed will have wide applicability for phase transformation studies. In particular, they will allow real-time experiments of phase stability and transformation to be designed and carried out in a microgravity environment.

Progress to Date: Realistic computer models describing nucleation and growth of a glass to a crystal of the same composition have been written and tested. Time-dependent nucleation rates and cluster-size-dependent growth velocities are included in a natural way. Using these programs hypothetical glasses have been prepared at different quenching rates. The subsequent crystallization behavior of these glasses is calculated under isothermal and nonisothermal annealing conditions. This computed crystallization behavior is compared with that found experimentally. Significant accomplishments to date include:

- (1) Quantitative fits to the transformation profiles obtained by nonisothermal DSC measurements for different scanning rates, using accepted values for nucleation and growth rates.
- (2) A predicted increase in glass stability (*i.e.* higher peak temperatures in DSC scans) with the quenching rate for the glass. Experiments are being carried out to check this.
- (3) A recent suggestion by Drs. Day and Ray that the temperature of the maximum nucleation rate and its magnitude can be estimated from DSC studies of glasses that were preannealed at different temperatures was investigated by numerically simulating the experiments. It was demonstrated that the suggested correlation is strongly dependent on the degree of overlap between the nucleation and growth regimes.
- (4) A demonstration that all existing methods for analyzing nonisothermal DSC data are fundamentally flawed for processes involving nucleation and growth. They give reasonably good values for the activation energies for transformations proceeding by growth only.
- (5) A demonstration that the growth velocity can be calculated using measured data for the transient times for nucleation. Besides providing a useful method for estimating these quantities, this demonstrates that the effective mobility for cluster attachment is the same for small and macroscopic clusters.
- (6) A demonstration of the importance of surface nucleation and growth in transformations in lithium disilicate glass; this is a point that was not previously appreciated.

Future Plans: Calculations are nearing completion for comparison with experimental devitrification data for lithium disilicate glasses that were scanned through the nucleation zone (defined as a region of significant nucleation) at different rates. Besides providing a further check on our numerical model, this may provide a new experimental method for estimating nucleation and growth parameters from DSC data. Similar calculations are being carried out for soda-lime-silicate glasses ($\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$) to investigate the importance of the degree of overlap between the nucleation and growth zones. Finally, calculations are being made for comparison with devitrification data from lithium disilicate glasses containing different populations of nucleating agents to investigate the effects of heterogeneous nucleation on glass stability.

Microgravity Science and Applications Division – Project Summary

Project Title: Glass Formation and Nucleation in Microgravity Containerless-Processed, Inviscid Silicate/Oxide Melts: Ground-Based Studies

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Project Identification Number and Contract Dates: NAGW-2835; 1 Dec. 1991–30 Nov. 1994

A. Task Objectives and Description

There are two specific tasks involved in this research project:

1. Nucleation by internal oxidation or reduction of transition metal-bearing silicate glasses and melts.

If a change in valence state of a transition metal cation within a silicate melt is associated with a change in its structural role within the melt, one might be able to affect internal, homogeneous nucleation within the melt via a change in the external environment, e.g., by a redox reaction. Critical to the hypothesis is the nature of transition metal cations to make the melt into a *semiconductor*: conduction electrons or electron holes are majority defect species and thus serve to decouple cation and anion diffusion fluxes that occur in an oxygen chemical potential gradient. One consequence is that oxidation or reduction reactions can occur *internally* (i.e., within the body of the melt) instead of solely on the surface. These reactions can result in the destabilization of the melt such that crystallization reactions occur in finely (nm-scale) dispersed regions of the melt body (e.g., the formation of Fe^{3+} -bearing spinel precipitates via the internal oxidation of an originally Fe^{2+} -bearing aluminosilicate melt). One can thus create fine-grained ceramics or glass-ceramics from what would normally be a non-glass-forming melts. Specific research involves control reaction experiments on silicate glasses and levitated reaction experiments (aero-acoustic and electrostatic levitation) on silicate melts.

2. Internal nucleation of inviscid pseudobinary silicate melts via metastable liquid-phase immiscibility.

Binary alkaline earth oxide-silicate melts are highly exothermic. Nevertheless, the structural variations between highly polymerized (silica-rich) and poorly polymerized (silica-poor) silicate liquids results in the creation of composition zones (on the silica-rich end of the phase diagram) where a single silicate liquid is not stable. On the silica-poor end of the diagram, this immiscibility would be *metastable*. As a consequence, if one can sufficiently undercool an inviscid, silica-poor silicate melt, one could perhaps cause metastable amorphous phase separation to occur prior to any crystallization. The phase separation could further promote the internal, fine (μm)-scale, uniform nucleation and crystallization of the material: the creation of unique glass-ceramic materials becomes a possibility. Scientifically, measurements of heat-evolution rate in such droplets will address questions concerning the role of amorphous phase separation in crystalline nucleation.

B. Comment on the Relationship of this Work to Microgravity Research

Both of the specific tasks in this research are critically dependent on *containerless* processing: in both cases, avoiding containers eliminates the most blatant source of heterogeneities that could promote heterogeneous nucleation. In the case of redox reactions (Task 1) the containerless requirement is additionally (and particularly) important in that chemical (as opposed to structural, e.g., nucleation) reactions can grossly affect the ionic-scale dynamics and structure of a transition metal-bearing melt. For example, noble-metal crucibles (e.g., platinum) that are often employed to contain refractory ionic melts will alloy with the transition metal ions incorporated in the melt: chemical diffusion different from that desired in the redox experiment results.

Microgravity comes into play as important when working with inviscid ceramic melts, specifically in the same two manners cited for dealing with molten metals: (1) density contrast amongst phases and (2) the need for quiescence. Both of these aspects are evident in our levitated melt drop experiments: melt viscosities of approximately 1 Pa·s (10 Poises) allow for shear-force-induced convection (droplets are far too small for thermal convection at this viscosity; processing of modestly larger melt bodies could promote thermal convection), which allows continuous exposure of new melt to the outside atmosphere thus short-circuiting the desired chemical diffusion process; in droplets avoiding convection, Ostwald ripening of internally formed ferrites allows them to sink to the bottom of the droplet, thus removing them from positions to act as internal nuclei for silicate phases.

C. Significant Results-to-Date and Future Plans

1. Nucleation by internal oxidation or reduction of transition metal-bearing silicate glasses and melts.

Oxidation experiments were completed on a suite of CaO-Na₂O-FeO-MgO-Al₂O₃-SiO₂ glasses (prepared from naturally occurring basalt) and on synthetic compositions minus the Na₂O. These experiments were analyzed by Rutherford backscattering spectroscopy (RBS), optical microscopy, transmitted electron microscopy (TEM) and high-energy electron diffraction (HEED). The RBS spectra clearly indicate that the oxidation process is accompanied by the flux of Ca²⁺, Mg²⁺ (both specimen types) and Na⁺ (natural basalt specimens) to the free surface, with the subsequent formation of a two-phase mixture of crystalline CaO and MgO that *partially covers the specimen surface*. Beneath this surface layer lies a depleted silicate glass that includes fine precipitates of MeFe₂O₄ spinel. The morphology of the reaction is consistent with the oxidation occurring by cation diffusion out of the glass. The kinetics are parabolic (diffusion-limited); the rate-limiting step for the oxidation/spinel nucleation process is thus diffusion of the divalent cations away from the reaction front towards the free surface. These experiments have been successfully extended to melts in two ways. Spheres of both the natural and synthetic compositions have been aero-acoustically levitated (AAL) and oxidized above the liquidus for the original melt composition. In the spheres so levitated that *remained quiescent*, the internal oxidation/nucleation process is plainly evident: internal homogeneous nucleation of magnesioferrite spinel (as well as ostwald ripening of these nuclei) and heterogeneous nucleation (on the spinel precipitates) of calcium-rich feldspar occurred. In similar experiments employing electrostatic levitation (ESL), the synthetic specimens were successfully levitated. Because of the limited capabilities of controlling the atmosphere in the ESL apparatus, a reduction reactions was promoted thermally. The process results in nucleation of pyroxenes on the specimen surface (on Fe metal nuclei) and an inward flux of metallic iron to so promote internal nucleation of silicates. Immediate future plans are to finish the development of the kinetic models to describe these phenomena and to characterize, via TEM and HEED, the crystalline nucleation process that occurs at the reaction front. Longer-term plans are the transfer of the idea from silicates to non-glass-forming oxides.

2. Internal nucleation of inviscid pseudobinary silicate melts via metastable liquid-phase immiscibility.

MgO-SiO₂ binary melts (metasilicate composition) have been drop-tube processed at approximately 1800°C. Yield of these experiments was surprisingly extensive: approximately 80 vol.% of the fine (<50-μm diameter) particles experienced melting in the process (a substantial increase in yield over powder processed at ~1600°C). We are presently collecting statistics on this processed powder, specifically discerning the amount of material that received sufficient undercooling so as to remain amorphous. We are further pursuing thermal analysis experiments on the amorphous powder to ascertain, if possible, the role of amorphous phase separation on the nucleation of glass-ceramic (i.e., spatially uniform, fine-grained crystalline) microstructure in these droplets. Time-resolved thermal analysis should allow discrimination of surface nucleation processes (i.e., heterogeneous nucleation on amorphous-amorphous interfaces) from possible homogeneous nucleation processes, as well as determine the scale of phase separation important to promote appropriate crystallization. We anticipate collecting such dynamic data and emphasizing its interpretation in 1994. Future plans include the extension of the work to a more inviscid system, Al₂O₃-SiO₂, which additionally has significant economic value (i.e., mullite ceramics) with successful melt processing to a glass-ceramic microstructure.

ELECTRONIC MATERIALS

In Situ Monitoring of Crystal Growth Using MEPHISTO

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A comprehensive directional solidification experiment was recently carried out successfully on the USMP-2 mission (STS-62) utilizing the MEPHISTO directional solidification facility. The 14 day shuttle flight was launched on Friday March 4, 1994. Using three samples processed in parallel, a total of 45 cm of dilute Bi-Sn alloys were solidified directionally in microgravity under well controlled and well characterized conditions. Prior to the final directional solidification, extensive measurements were performed on the samples, consisting of Seebeck measurements to measure the solid/liquid (s/l) interface temperature, resistance measurements to track the position of the s/l interface and thermal gradient measurements in the solid and liquid during freezing and melting. The final solidification also included a procedure for marking the shape of the s/l interface via mechanical perturbations, as well as rapid quenching of a 2 cm section of one of the samples.

The experiments were performed to gain a detailed understanding of the role of gravity driven convection during the solidification of faceted materials. Two fundamental and interrelated aspects of the liquid to solid transformation have been investigated: (a) morphological stability of the solid/liquid (s/l) interfaces and the resulting macro- and micro-segregation patterns and (b) atomic attachment kinetics at the freezing interface, deduced via measurement of the growth rate-interface supercooling relationship(s).

This research program was initiated in January 1990 by the University of Florida (UF) as a collaborative effort involving the Centre d'Etudes Nucleaires de Grenoble (CENG), the Centre National d'Etudes Spatiales (CNES) and the National Institute of Standards and Technology (NIST). The funding for the project was provided by MSAD, with the NASA project management from the Lewis Research Center.

In order to achieve the goals of the project in the relatively short period from its initiation in '90 to the launch in March 1994, a three-pronged strategy for achieving the stated goals was used: (a) Development of experimental apparatus for ground based kinetics and morphological stability studies at UF, (b) Scientific and technical collaboration with the MEPHISTO teams at CENG and CNES and (c) Analytical modeling of morphological stability and interface kinetics in collaboration with Sam Coriell (NIST). Particular reference is also made to an extensive collaboration between the various scientific and technical personnel from NASA-Lewis for developing a comprehensive flight program.

Within this framework, the research team at UF developed the facilities necessary for ground based experiments to ensure maximum conformity with the MEPHISTO space hardware. In addition, four "campaigns" were conducted prior to the USMP-2 mission (three on the MEPHISTO engineering model at CENG and one on the MEPHISTO flight model at CNES). Each campaign required three samples approximately 1 meter in length, which were prepared at UF according to MEPHISTO specifications. The campaigns not only proved the integrity of the samples produced, but also provided valuable ground based data, which is currently being compared with the flight experiments. Concurrently, NIST has carried out

analytical modeling of the morphological stability of faceted solid/liquid (s/l) interfaces for the alloy system under investigation.

These flight experiments utilized a novel technique (termed the Seebeck technique) to measure the interface supercooling directly, non-invasively and *in-situ* (i.e. in real time during growth). The interface velocity was measured by monitoring the resistance change across the sample, while the interface shape was delineated by subjecting the sample to electrical current pulses (for ground based studies) and mechanical perturbations (for μ -g studies) to cause a momentary demarcation of the interfaces.

Initial ground-based experiments were carried out using high purity Bi and dilute Bi-Sn alloys. Bi-Sn alloys were chosen to complement the experiments conducted by CENG/CNES on the first flight of MEPHISTO (MEPHISTO-1): on this flight, dilute, non-faceted Sn-Bi alloys were used, while this research program (the second flight of MEPHISTO, or MEPHISTO-2) used strongly faceted Bi- 0.1 at.% Sn alloys. In this manner, the results of the two flights are being used to compare and contrast various fundamental aspects of solidification without and with a strong influence of atomic attachment kinetics, respectively, in the presence (ground-based studies) and near-absence (μ -g studies) of gravity induced convection. It is expected that this comprehensive investigation approach will significantly further our understanding of key crystal growth parameters.

We further expect to use these data to test and improve many of the current solidification theories. In particular, the interplay between morphological stability and interface kinetics is not well understood at the present time. The microgravity experiments will yield an integrated database involving interface velocity/interface shape/interface supercooling. Such data are important from both practical and theoretical standpoints. For example, a knowledge of the transition from a faceted to a rough interface (from the Seebeck data) and the interface shape (from solute-dump-demarcated interfaces) under identical growth conditions has important applications in practical crystal growth situations: the information can be used to understand the correlation between defect generation and solute banding. In addition, because the information has been obtained in diffusion dominated conditions without the overriding effects of gravity-induced thermo-solutal convection, meaningful tests (and appropriate refinements) of the current crystal growth theories can be made.

Two other spin-offs of the proposed program are worthy of note here: we will be able to obtain values of key parameters, such as liquid diffusivities, via this investigation. In addition, the novel and non-intrusive technique used to measure the interface temperature can potentially be utilized for monitoring and controlling the space-based single crystal growth of technologically important semiconductors.

We are currently analyzing the approximately 6 gigabytes of USMP-2 MEPHISTO data. During the mission, extensive use was made of the telemetry commanding capability to modify and refine experimental procedures for better scientific yield. Preliminary analysis of the data acquired during the first 28 hours of mission shows excellent correlation of the Seebeck signal with melting/freezing as well as solute build-up/decay. Numerical calculations are being carried out concurrently to correlate the seebeck signal with thermal/solutal decay and hence to back calculate an accurate value of the diffusion coefficient of tin in liquid bismuth.

Summary

Solution Growth of Crystals in Low Gravity

NASA Contract NAS8-36634
Microgravity Science and Applications Division
NASA Headquarters, Washington D.C.

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James D. Trolinger, MetroLaser, Irvine, CA.
William R. Wilcox, Clarkson University, Potsdam, NY.

Objectives

The objectives of the experiment were: (a) to grow crystals of triglycine sulfate (TGS) in low gravity by low temperature solution crystal growth technique using the modified Fluid Experiment System (FES); (b) to map the three dimensional concentration field around the growing crystal with holographic tomography ; (c) to study the fluid motion due to residual g and g-jitter by using multiple exposure holography of tracer particles; and (d) to study the influence of g-jitter on the crystal quality and the growth rate.

Benefits of Microgravity

If convective mixing of reactant solutions occurs , then massive nucleation and rapid growth take place, resulting in small, poor-quality crystals. On earth, convective mixing can be avoided only by using very thin contacting regions or by use of a gel. Sizable crystals have been grown by use of gels, but unfortunately, a suitable gel does not exist for many precipitation systems; in others the gel contaminates the crystals. In space, the precipitating solutions can be allowed to diffuse together without the requirement for a gel to avoid convective mixing. Experiments on Spacelab-3, IML-1, and other missions have shown very promising results for solution crystal growth of optical and protein crystals.

Importance of TGS crystals

TGS and its derivatives are the most sensitive ferroelectric materials widely used for infrared detectors operating at room temperature. The devices based on TGS require crystals of high optical quality. The detectivity (D^*) of the best TGS detectors available today is more than one order of magnitude below the theoretical background limit. The limitation has been attributed to the dielectric loss and other defects in the crystal. The sources of the dielectric loss are usually attributable to microscopic inclusions, pinning of domains by defect centers, and other defects caused by buoyancy driven convection. Therefore, it should be possible to reach near the

theoretical limit of D^* , if inclusion free crystals can be grown.

Description of the experiment on the First International Microgravity Laboratory (IML-1)

An experiment, "A study of solution crystal growth in low-g," was flown on STS-42 aboard the First International Microgravity Laboratory (IML-1) on January 22-29, 1992. A crystal of triglycine sulfate (TGS), $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$, was grown from aqueous solution using a specially developed for space cooled sting technique incorporated in the modified FES. The total time for the experiment run was approximately 18h. The seed crystal was a faceted/natural TGS seed. Particle image displacement velocimetry (PIV) was used to monitor convection in the crystal growth cell. The positions of polystyrene spheres of three different sizes, 199, 468, and 646 microns suspended in the growth solution, were recorded by holography at intervals throughout the experiment. The recorded motion of the suspended particles was used to trace the fluid motion. During the experiment, an optical system of the FES provided holograms and schlieren images of the process as it progressed in the growth cell. Based on the digitized images reconstructed from the holograms, the motion of the particles in the transparent TGS solution could be tracked.

Significant Results

The growth on the (010) face of the TGS crystal was substantially more uniform over a period of 18h as compared to a typical ground grown face. The local acceptance angle for diffraction of monochromatic synchrotron X-radiation from the uncut crystal, 1-2 arc second, indicates extraordinary crystal regularity. Observation of the cut edge of the flight crystal (TGS-1) show continuity between the seed at the bottom and the space growth at the top, indicating a high degree of epitaxy of the space grown material. The demarcation between the seed and the space grown material is indistinct, indicating a smooth transition from dissolution to growth. This condition is not common in ground grown crystals.

The infrared detectors fabricated from the TGS-1 flight crystal show improved detectivity (D^*) compared to ground samples and even with detectors fabricated from the crystals grown on Spacelab-3 in 1985. The dielectric loss in the IML-1 crystal is lower than in ground crystals and in crystals grown in Spacelab-3.

The motion of three different size particles has been tracked. A random walk phenomenon has been observed and quantified. The particle motion does not obey a simple g-jitter model. The effects of g-jitter on particle motion cannot be described with a uniform body force varying with time in the equations of motion. The contradiction between the theory and the observed results lead to a doubt that either the g-jitter was not only function of time but also function of the spatial coordinates or, some of the particles were driven by vibration. Theoretical results on convection and growth kinetics indicates that the orientation of residual g makes big difference to growth morphology. The higher the frequency of g-jitter the less the effect on growth rate. These observations have important implications on materials processing in space.

Summary of NASA Sponsored Research Program

Modelling of Convection and Crystal Growth in Directional Solidification of Semiconductor and Oxide Crystals

NASA Grant: NAG8-961
Principal Investigator: Robert A. Brown
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Date: April 30, 1994

Summary

Fundamental understanding of the interactions of heat, mass and solute transport on the quality of crystals grown from the melt is important in the design and control of systems for crystal growth in a microgravity environment and the interpretation of results from these experiments in the context of earthbound experience. Much of this understanding will come from comparison of experiments in both terrestrial and microgravity conditions to high-quality numerical simulations that are designed to describe, as quantitatively as possible, the transport processes and solidification in each system. The research program described here focuses on the development of the computational tools for detailed analysis of the vertical Bridgman crystal growth system for the growth of both semiconductor and oxide crystals. The research links several components to accomplish these goals. The first is the development of very accurate and efficient methods for the computation of diffuse-gray radiation in the furnace enclosure and of radiation in a semitransparent material for the case of oxide growth. The second is the development of advanced computational methods capable of computing three-dimensional convection in the melt coupled with realistic furnace models for analysis of melt convection during growth under terrestrial and microgravity conditions. These algorithms will be based on the application of finite element methods for the solution of the integrated heat transport and convection models for vertical Bridgman growth using MIMD parallel computers.

Research in the first year has been directed toward the development of computational tools needed for the vertical Bridgman simulator described above. To date the following developments have been made:

1. A new object-oriented method for the computation of view factors for axisymmetric, diffuse-gray radiation has been developed.
2. The basic elements of a parallel implementation of the finite-element/Newton method for solving transport problems has been completed and demonstrated for buoyancy-driven convection.

A vertical Bridgman crystal growth simulator that incorporates the new, diffuse-grey radiation calculation, irregular, adaptive finite-element meshes, and the Newton iteration is being developed for simultaneous solution of the solidification and conjugate heat transfer problems. The simulator is initially being applied to the modelling of the crystal growth of Bismuth Germanate, BGO, a scintillating oxide material used in detector applications. Support from this NASA program also has been used to complete a previously begun analysis of the small-scale floating zone system. Accomplishments in each of these areas are described briefly below.

Object-Oriented View Factor Calculation

Accurate calculation of view factors for use in the diffuse-grey radiation calculation is one of the most important elements of calculation of high temperature radiation in crystal growth systems. Two features of the numerical method are needed to insure accuracy of the radiation calculation: fine finite element surface discretizations and accurate calculation of the view factor from one surface element to another. Most previous calculations of crystal growth furnaces use some form of the Facet algorithm first modified by us for this application. Here the view factor from any flat surface element to any other is computed by a double area quadrature, once the possibility of blocking by another surface element is tested for each element. The computation of the blocking is the most time intensive part of the algorithm, scaling as $O(N_s^3)$, where N_s is the number of surface elements in the radiation enclosure.

We have developed an object-oriented method (OOM) that takes account of the axisymmetry of typical furnace geometries and that groups surface elements into conical and cylindrical objects, thereby drastically reducing the blocking calculation. The OOM is based on Nusselt's projection method for computing view factors by projection on the surface of a hemisphere. The OOM method scales as $O(N_{obj} N_s)$, where N_{obj} is the number of objects in the enclosure; usually $N_{obj} \ll N_s$. Simulations for model systems and for realistic crystal growth furnaces have verified this scaling. The OOM method and applications to crystal growth systems are described in [1].

Parallel Implementation of the Finite-Element/Newton Method

Robust numerical solution of very detailed simulations of crystal growth furnaces and three-dimensional convection in the melt present computational problems that are at the leading edge of supercomputing today. To advance these simulations will require the application of parallel computing to the solution of the physicochemically complex transport models that are needed to model crystal growth systems. A major goal of this program is the development of a finite-element based methodology for this purpose. Our approach is to use finite element methods to reduce these models to large systems of algebraic equations and to solve these equations by Newton's method. Each Newton iteration requires the solution of a large set of algebraic equations which is the heart of the algorithm. We do this by LU decomposition using domain decomposition and nested-dissection to distribute the work of LU decomposition over the multiple processors of a MIMD parallel computer. Our implementation of LU decomposition is described in [3] and is among the fastest algorithms of its type available. We have used this algorithm to solve model problems in steady-state and transient buoyancy-driven flow and have demonstrated the robustness of the algorithm, as well as the linear speed increase of the algorithm with increasing number of processors; these results are described in [4,5]

Dynamics of Small-Scale Floating Zones

Small-scale floating zones are used in a number of microgravity experiments and offer a very interesting case study in the dynamics of meniscus-defined crystal growth. The goal of this project has been to develop detailed models and numerical simulation tools for the analysis of steady-states, their stability, and nonlinear dynamics of small-scale floating zones. The thermocapillary models include both steady-state and transient analysis of heat transfer in all phases, convection in the melt, the shapes of the melt/crystal and melt/feed-rod interfaces and the shape of the meniscus. Finite-element analysis is used to discretize the model and Newton's method is used to solve the nonlinear algebraic equation set that arises in the steady-state calculation and at each time-step of a fully implicit time integration. Zone stability is tested by linear stability theory implemented in the finite-element formalism using an Arnoldi algorithm to

compute the most dangerous eigenvalues of the linear stability problem for each set of operating conditions. Our initial results described in [2] describe the dynamics of the zone in the absence of convection in the melt. Here the interplay between surface tension, which limits the zone length through the Rayleigh limit, and heat transfer are shown to lead to a new oscillatory mode for instability in the floating zone shape in which the zone length oscillates with growing amplitude until the zone breaks. This instability occurs before the maximum zone length that is predicted by the Rayleigh limit for an ideal cylindrical zone. The Rayleigh limit is systematically tied to the lost of existence of steady-state solutions for zones with gravity.

List of Publication

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2. Covert, H. and Brown, R.A., Dynamics of a small-scale floating zone: the thermal-capillary limit. *J. Fluid Mech.* in preparation (1994).
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4. Mehrabi, R. and Brown, R.A., Finite-element/Newton method for solution of nonlinear problems in transport processes using domain decomposition and nested dissection on MIMD parallel computers. *Proceedings of the Seventh International Meeting on Domain Decomposition*. American Mathematical Society, in press, 1994.
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DOUBLE DIFFUSIVE CONVECTION DURING GROWTH OF LEAD BROMIDE CRYSTALS IN SPACE

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Contract No.: NAS3-25811

1. PROGRAM OBJECTIVES

The main objective of this program is to evaluate, understand and eliminate thermosolutal convection during the crystal growth of $\text{PbBr}_2\text{-AgBr}$ system. The program will provide a quantitative understanding of convective effects and a correlation of experimental data with theories developed for thermosolutal convection will be carried out. For the $\text{PbBr}_2\text{-AgBr}$ system less dense solute causes the convective (thermosolutal) instability in addition to morphological instability. Also, this system is optically transparent and we can monitor the interface shape to study the convective and morphological instabilities. The scientific and technical objectives are listed as follows.

1.1 Scientific Objectives:

The scientific objectives of this program are to understand the thermosolutal convection during the crystal growth of the $\text{PbBr}_2\text{-AgBr}$ system. This will be achieved by growing five crystals at five different concentrations, which will lead to different solutal convective levels. The experimental values of the concentration distribution will be compared with the theories based on pure diffusional growth to evaluate the effect of convection. Also, numerical studies will be carried out to study the convective and morphological instabilities, and to determine the critical concentration of dopant for a particular growth velocity and gravity level. Theoretical instability diagrams will be compared with the experimental studies. Relevant analytical characterization techniques are to be used to evaluate the effect of convection on crystal quality. These studies will provide basic data on convective behavior in doped lead bromide crystals grown by the commercially important Bridgman process. These objectives will be met by following tasks:

- Distribution of dopant will be studied in 1-g grown crystal to understand thermosolutal convection and its effect.
- Diffusion coefficient will be measured and compared with values predicted by the crystal growth experiment.
- The ratio of thermal conductivities will be determined experimentally. These data along with diffusion coefficient will be used to predict the theoretical stability diagrams.
- The convecto-diffusive theory will be examined by growing crystals at a fixed growth velocity and comparing the experimental solutal redistributions. One crystal will be grown at different velocities to evaluate the boundary limits of morphological theories.

- To evaluate quantitative improvements in crystal quality with varying convective levels X-ray rocking curves, X-ray contours and etchpit techniques will be used to evaluate the homogeneity of crystals.

1.2 Technical Objectives:

The technical objectives of this programs are to define the parameter at normal gravity to minimize the thermosolutal convection during growth of doped lead bromide crystals to achieve homogeneous distribution of dopant, significantly reduce the optical and acoustic scattering caused by convection during lead bromide crystal growth, and produce lead bromide crystals with unparalleled optical homogeneity for advanced device applications. This will be achieved by experimentally verified stability diagrams and direct observations on solid-liquid interface during crystal growth.

2. NECESSITY FOR MICROGRAVITY

Preliminary results of numerical calculations on stability diagrams and crystal growth at different Rayleigh numbers indicate that diffusion controlled growth is essential to achieve the optical homogeneity. There is a limit to lower for the aspect ratio and temperature gradient, however, we cannot lower the Rayleigh number required to grow a cm size crystal. Lead bromide crystals of 13 mm diameter and 6 cm in [010] orientation are required to fabricate a Bragg cell of 100 microsecond delay time. On the other hand, going from 1-g to 10^{-4} g lowers the Rayleigh number by four orders of magnitude, which is sufficient to reduce the convection to the desired level to achieve high homogeneity.

3. SIGNIFICANT RESULTS

We are using a diaphragm cell technique to experimentally determine the true diffusion coefficient of PbBr_2 -AgBr system. For this task we had to determine the cell constant β given as:

$$\beta = A(V_R + V_L)/V_R \cdot V_L \omega,$$

where ω is the thickness of the membrane, A is the cross section area, and V_L and V_R are the volumes of left and right chambers. The cell constant is determined experimentally by using water and potassium chloride solution. A set-of five experiments showed that cell constant is 0.20. At present we are carrying out diffusion measurements of PbBr_2 and AgBr at a temperature above 375°C . The final concentration will be used to evaluate the diffusion coefficient.

We have finished the experimental measurements of the ratio of thermal conductivities. After we complete the diffusion coefficient measurements, we will start calculating critical concentration for different growth velocity and at different g-level.

We have started growing a single crystal with 5000 ppm AgBr dopant. After the completion of the growth run, solute distribution will be determined and experimental data will be compared with theories. The crystal quality will be also determined by using different techniques. This will be 1-g baseline data to compare with the crystal grown in microgravity environment.

CRYSTAL GROWTH AND SEGREGATION USING THE SUBMERGED HEATER METHOD (NAG8-952)

Research Report Summary

Submitted to

National Aeronautics and Space Administration

(2/1/93 to 5/31/94)

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INTRODUCTION

The Submerged Heater Method (SHM) used in this project is a variation of the vertical Bridgman (VB) method. The main feature of the Submerged Heater Method is a disc-shaped member, immersed in the vertical Bridgman melt, Fig.1. The submerged "heater" or "baffle": i) allows temperature measurement ~ 1 cm from the freezing interface, ii) reduces the destabilizing radial temperature gradients in the melt, and iii) acts as a convection baffle [1].

Buoyancy driven convection in a melt is drastically reduced. The ratio between buoyancy and viscous forces in the melt (i.e., the Rayleigh number) is reduced for a factor of $\sim 10^4$, a reduction compatible to that of reducing the gravitational acceleration to 10^{-4} of the earth gravity.

(1) OBJECTIVES

Fundamental studies of solute segregation at low levels of melt convection are conducted using a programmable multi-zone furnace (PMZF) modified for growth by the Submerged Heater Method. The ground-based experimental work is accompanied by numerical simulations. The specific objectives of these studies are to:

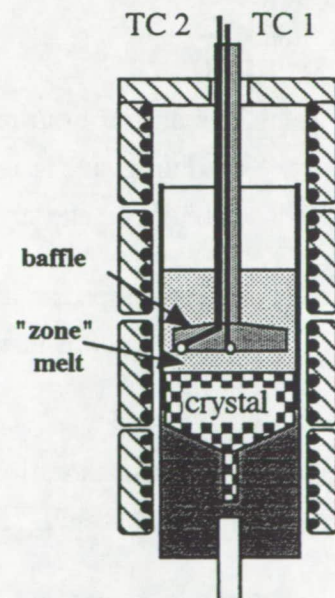


Fig.1 Schematic of the Submerged Heater Method

- Evaluate the suitability of the multi-zone furnace with the submerged heater to serve as a ground-based solidification facility, useful for pre-and post-flight studies.
- Seek explanations for previous space experiments not demonstrating the diffusion controlled segregation.
- Study the response of various dopant-melt systems to low levels of convection; determine the criteria that will allow the diffusion-controlled segregation.
- Evaluate the benefits of using the SHM within a PMZF for future space experiments;
- Design a submerged heater that can be used within the PMZF in future space growth experiments.

(2) RELATIONSHIP TO MICROGRAVITY RESEARCH

We hope to demonstrate that the multi-zone furnace with the submerged heater is useful for pre-and post-flight studies. The pre-flight studies may help to optimize the future space experiments.

Our current "post-flight studies" focus on solvent-solute systems previously used in space (doped Ge and InSb). We hope to explain why some space experiments did not result in diffusion controlled segregation.

(3) RESULTS

The thrust of our research during the first year of the NASA sponsorship is directed at modeling and consolidation of the experimental basis for crystal growth by the Submerged Heater Method.

We developed an axisymmetric model of heat and species transfer which allows studies of segregation in vertical Bridgman configuration, with and without the submerged heater.

Numerous modifications were made on the programmable multi-zone Mellen furnace. The furnace was calibrated and one growth experiment was conducted.

A transparent two-zone Bridgman furnace was designed and built. The experiments in the transparent furnace are helping us to reveal the melt convection, the shape and the position of the growth interface during growth by SHM. Furthermore, this furnace is being used to develop a submerged baffle that can be used in sealed ampoules.

Publications:

- [1] A. G. Ostrogorsky, G. Müller, *J. Crystal Growth* 137 (1994) 64-71 (Invited talk at ACCG-9, Baltimore, August 1993).

SUMMARY REPORT:

IDENTIFICATION OF GRAVITY RELATED EFFECTS ON CRYSTAL GROWTH, SEGREGATION AND DEFECT FORMATION IN BSO ($\text{Bi}_{12}\text{SiO}_{20}$)

A.F. Witt NASA Grant NAG8-949
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The current on-going research program on growth and characterization of BSO places focus on a class of materials (optical and opto-electronic) with theoretical properties that are outstanding, but which have so far failed to reach their potential primarily because of our inability to adequately control during growth their stoichiometry, incorporation of functional minority constituents, crystal defect formation and confinement related contamination. Theoretical considerations indicate that the majority of existing growth deficiencies, which are responsible for our inability to produce viable device structures, are directly or indirectly related to gravitational effects. Thus it appears that an assessment of the true potential of selenites, which exhibit outstanding piezoelectric properties and exceptionally light optical rotative activity in device application, can at this time best be made on material obtained from controlled growth experiments in a reduced gravity environment. Under such conditions convective interference, otherwise unavoidable, is projected to be substantially suppressed and defect structures resulting during growth are expected to approach equilibrium values. Magnetic melt stabilization, found effective in growth of semiconductors, is ineffective in oxide systems.

Knowledge gained from space experiments and the related ground-based program is expected to advance the science base for crystal growth of oxides and thus to narrow the still existing gap between theory and experiment. More specifically, the proposed program provides an approach to the deconvolution of the effects of largely uncontrolled, complex processing variables on crystal growth and segregation, leading to the identification of growth conditions by which device specific property requirements in oxides can be approached. Such growth conditions are expected to be realizable in a modified Bridgman growth geometry, the subject of development in the ground-based support program.

The research to date has focused on (a) the development of BSO single crystal growth capability by the Czochralski technique, (b) the characterization of growth and defect formation in BSO, and (c) the development of a "Bridgman-type" growth

configuration of BSO that permits enhanced heat transfer control under quantifiable thermal boundary conditions and which is functionally compatible with NASA-generated existing hardware. (The establishment of quantifiable growth conditions and the *in situ* growth characterization capability by means of current induced interface demarcation are considered essential in efforts directed at assessing the potential of reduced gravity environment for crystal growth research and development since the customary empirical approach is considered prohibitive.)

Crystal Growth of BSO: A heat pipe-based Czochralski system, providing for a controlled ambient atmosphere and current induced growth interface demarcation, has been established and used extensively to grow material from which growth and segregation effects in conventional operation are being determined.

Characterization: In view of extensive experience in optical characterization gained from NASA-sponsored research of III-V and II-VI compound semiconductors, existing facilities for optical transmission microscopy and related computational image processing and analysis were modified to permit the characterization of oxides.

To determine the basic growth features of BSO, Ga-doped as well as undoped crystals using charges ranging from 50-70g were grown and analyzed. It was found that (1) rotational striations are absent in crystals grown with the heat pipe based system; (2) non-rotational striations, highly periodic in nature and exhibiting two distinctly different frequencies, are present in both the core and off-core regions; (3) the frequency of striation formation appears to be a weak function of the aspect ratio of the charge, independent of the rate of seed rotation and not noticeably dependent on the rate of crystal pulling; (4) the primary crystal deficiencies are gaseous inclusions; their appearance is a function of both the rate of crystal rotation and the rate of crystal pulling; (5) generation of dislocations is found to be predominantly related to inclusion of "gas bubbles"; (6) dislocations have been made "visible" through decoration by annealing in a reducing atmosphere; and (7) current induced interface demarcation has been successful – its formation can be attributed to Joule heating rather than a Peltier effect.

Design of Bridgman Facility: A heat pipe based Bridgman facility has been designed and constructed. The system is equipped for interface demarcation and will provide growth rate as well as thermal gradient stabilization. It is currently being tested for performance characteristics using a "graphite charge" and will subsequently be used to establish growth conditions for BSO in vertical configuration.

Combined Heat Transfer Analysis of Crystal Growth

Principal Investigator:

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April 1993

1. Objective

The technical objective of this research effort is to provide a quantitative understanding of the role of radiation heat transfer on crystal growth in low-gravity space experiments. To accomplish this goal a generalized combined conductive-convective-radiative numerical model is developed which can accommodate various crystal growth experiments.

2. Microgravity Aspect

Radiation heat transfer affects crystal growth in both space and ground-based processing. This is due to the high operating temperatures of the crystal growth processes, the semi-transparency of the crucible and phase change materials and the heat transfer link between the crucible and the furnace. In ground-based experiments, radiation and convection coexist and compete for dominating the heat transfer process in the ampoule. The role of radiation, however, becomes more prominent in low-gravity environment of space where convection heat transfer is considerably minimized. Low gravity numerical simulations clearly indicate that radiation effects are dominant during solidification of two important oxide crystals, BSO and YAG, and determine the shape and movement of the growth interface.

3. Approach

A numerical methodology was developed for radiation exchange in the generalized multi-dimensional cylindrical geometries encountered in crystal growth. The radiation scheme which is based on the Discretized Exchange Factor method (DEF) uses node-to-node exchange to calculate radiation heat transfer in an absorbing emitting scattering nongray medium. One of the advantages of this radiation model is that it can be easily incorporated into existing finite difference or finite element codes.

The validity and accuracy of the radiation scheme was tested by comparing results to benchmark limiting solutions available in the literature [1]. The radiation model was incorporated into a finite element code for fluid flow and heat transfer and a generalized radiation-convection-conduction model was developed for crystal growth in cylindrical

ampoules. The solution algorithm tracks the movement of the interface during the solidification process and adjusts the finite element mesh to accommodate changes in the shape and position of the growing solid. Radiation view factors are also continuously updated as the geometry is altered

4. Results

Combined heat transfer and fluid flow models were developed for solidification of two oxide crystals BSO (bismuth silicate) and YAG (yttrium aluminium oxide garnet). Both crystals are transparent to radiation below 6 microns and opaque to radiation in the rest of the spectrum. The models are based on actual experimental configurations and conditions and include the effects of the furnace and the crucible wall. Results of numerical simulations which are also corroborated by qualitative experimental evidence clearly indicate that solidification of both BSO and YAG is greatly influenced by thermal radiation [2]. The shape and position of the interface can be grossly misrepresented if radiation effects are neglected.

In low-gravity experiments, radiation loss through the semitransparent solid dominates the heat transfer at the solidification front for both materials and results in a highly stretched parabolic interface shape which protrudes convexly into the melt. As a result, the fluid flow pattern is also substantially modified.

In 1-g solidification of BSO, convection in the melt also plays an important role. In this case, heat transported by the recirculating vortices near the interface produces an interface which is much flatter than in the corresponding low-g case.

Numerical experiments also indicate that because of the dominant role of radiation during solidification of semi-transparent crystals such as BSO and YAG, a flat interface shape can only be achieved by minimizing the net radiative loss from the interface through the solid. This is valid for both 1-g and low-g applications

5. Future Directions

The study will be extended to include other oxide and semiconductor crystals with transparent bands. Effects of different crucible materials and furnace profiles will be investigated. A Monte Carlo radiation model will be developed to investigate the intricate effect of variation in the index of refraction across the interface.

6. References

1. Kassemi, M., and Naraghi, M.H.N., 1993, "Analysis of Radiation-Natural Convection Interactions in 1-g and Low-g Environments Using the Discrete Exchange Factor Method", *Int. J. Heat and Mass Transfer*, Vol. 36, No. 17, p. 4141.
2. Kassemi M., and Naraghi, M.H.N., 1994, "Combined Heat Transfer and Fluid Flow Analysis of Semi-Transparent Crystals in Low-G and 1-G Solidification", Numerical Modeling of Solidification Processes, *Proceedings of the 1994 ASME Winter Annual Meeting*, Chicago, Illinois.

Fundamentals of Thermomigration of Liquid Zones Through Solids

Summary Prepared for the
1994 NASA Microgravity Materials Science Program Review

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Introduction

A fundamental study of thermomigration of liquid zones through solids, using the rather unique technique of temperature gradient zone melting (TGZM), is underway at the University of Florida. The current experiments are focused on gaining a more detailed understanding of the role of interfacial atomistics and interface morphology upon crystal growth at temperatures well below the melting points of the candidate materials. The ultimate goal is to propagate low melting point liquids through relatively complex compounds with significantly higher melting points (e.g., Al/MoSi₂ and Ga/NiAl). Our initial studies have focused on the propagation of aluminum through silicon, chosen for simplicity relative to the more complex systems.

Scientific Background

TGZM is a relatively novel and significantly underutilized technique of moving a liquid zone through a solid, first published by Pfann in 1955. A thin layer of low melting point solute (B) is sandwiched between two blocks of higher melting point solvent (A) and the assembly is subjected to a temperature gradient. If the lowest temperature is above the melting point of B and the highest temperature is below the melting temperature of A then the layer of solute will melt and dissolve some A. The molten zone will move in the direction of the temperature gradient as A atoms dissolve at the hot interface, diffuse through the zone and redeposit as a crystalline layer of A at the cold interface. If the lower block of solvent A is a single crystal seed, this technique can be used to transform the upper block of A into a single crystal of the seed orientation. In order to obtain a uniform composition in the solidified metal, the cool interface must be maintained at a constant temperature. This can be achieved by monitoring the position of the zone using ultrasonic techniques which provide feedback to the temperature control system.

It should be noted that there are two factors contributing to the driving force for thermomigration of the liquid zone, namely the temperature gradient and the liquid zone composition gradient. Natural convection in the zone results in convective mixing of the liquid as gravity drives the higher density liquid downward and allows the lower density liquid to rise. This mixing process tends to reduce the concentration gradient in the zone and limit the driving force for thermomigration primarily to that due to the temperature gradient. Experiments conducted in a microgravity environment would provide the opportunity to evaluate the effects of convective mixing by reducing the gravity vector and concentrating on the contribution of diffusion via the temperature gradient.

Results to Date

The initial experiments designed to conduct these studies were performed using a vertical tube furnace with an applied temperature gradient inside of an argon-purged dry box. The success of the initial attempts to propagate an aluminum zone through solid silicon was limited by considerable problems encountered with oxidation. The surfaces of the aluminum foil were sufficiently oxidized such that, upon melting, the oxide layers precluded the liquid aluminum from adequately contacting the silicon surfaces. In one instance, the liquid aluminum "leaked" out the side of the zone and formed a droplet on the side of the silicon block. Examination of this sample after heating for 72 h showed that the aluminum actually underwent thermomigration up the side of the upper silicon block. This result demonstrated that it is possible to propagate aluminum through silicon when the oxidation at the surfaces is controlled and that it is necessary to limit the oxidation of the aluminum during the process.

In an attempt to reduce the oxidation prevalent during the initial thermomigration attempts, the temperature gradient furnace was redesigned so that it could be evacuated to high vacuum and then backfilled with purified argon to provide an inert atmosphere during processing. In order to establish more intimate surface contact and reduce oxidation, the silicon and aluminum samples were stacked between two stainless steel discs and compressed by two bolts while immersed in a methanol bath.

Upon examination of one set of samples after heating for 35 h, it was observed that the liquid aluminum had not "leaked out" of the zone between the two silicon blocks during the experiment. Some areas of the silicon-silicon interface appeared to have welded together, with no visible gap existing between the two blocks. The sample was cut longitudinally to evaluate the position and structure of the zone. It is evident from the photomicrographs presented in Fig. 4 that the aluminum zone moved up the temperature gradient approximately 3 mm (1/8 in.). The aluminum solvent zone appears to be rather discontinuous across the diameter of the specimen. This lack of stability may result from the solvent traveling along the grain boundaries intersecting the leading edge of the molten zone. The original interface position marked A in Fig. 4 also shows a lack of annihilation of the interface as would be expected if true epitaxial regrowth had occurred during TGZM. Thus, while TGZM in this system is possible, it is necessary to control oxidation carefully.

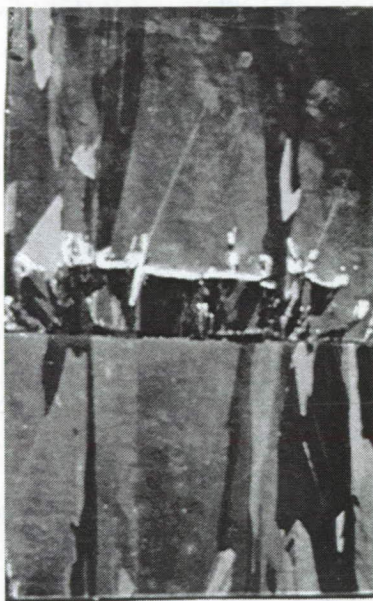


Figure 1. Photomicrograph showing the thermomigration of an aluminum zone through solid silicon.

Future Work

After fully establishing that the selected zone materials will propagate through the solids of interest, the focus of the research effort will concentrate on monitoring the interface positions and measuring the actual liquid zone temperatures. This will be achieved by utilizing ultrasonic methods and Seebeck techniques to measure the interface positions, zone lengths, and interface temperatures. This information will be used as input to a computer system which will control the furnace temperature, thus providing a means to maintain the cold interface at a constant temperature as is required for producing uniform compositions of the solidifying metal. Thus, our current plans are to develop a ground-based system which will require movement of the sample relative to the furnace such that the interface temperature may be held essentially constant during processing. Once this system has been developed, it will be necessary to study the transport phenomena within the liquid zones which govern their stability and motion. Determination of the rate controlling step for interface motion under gravity as well as the stability and coherency of the traveling solvent zone is imperative in order to prepare for a possible microgravity environment.

Numerical Investigation of Thermal Creep and Thermal Stress Effects on Microgravity Physical Vapor Transport

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Research Summary

Crystal growth by Physical Vapor Transport (PVT) is the process by which an amorphous solid is vaporized at one end of a cylindrical ampoule, transported across the ampoule by diffusion and convection and deposited at the other end as a crystal. In microgravity (μg) environments buoyancy induced convection is largely eliminated, and the reduction in transport rates under this condition has been shown to lead to significant and unexpected improvements in crystal structure and quality.

An accurate means of predicting mass transfer in μg PVT processes is important in view of the considerable cost of performing experiments. Although diffusion is widely regarded as the dominant transport mechanism in the μg environment, additional mechanisms which are negligible in the presence of buoyant flows may become significant in the highly nonisothermal conditions of PVT ampoules. Consideration of several of these mechanisms is the subject of this study.

One such mechanism is thermal creep, which is the slip flow over a surface resulting from a tangential gas temperature gradient adjacent to the surface. A simple explanation of this effect recognizes that gas molecules originating from the high temperature regions will impart a higher momentum when striking a surface than those originating from the low temperature regions. The surface responds to the uneven momentum transfer by 'pushing' the fluid towards the higher temperature gas. On a phenomenological level, the slip velocity will be proportional to the temperature gradient and the kinematic viscosity of the gas and inversely proportional to the absolute temperature.

As a first effort towards predicting the effect of thermal creep on μg PVT processes, a simplified model of diffusive/convective PVT in a cylindrical ampoule, including thermal creep, was examined¹. Following the conclusions of previous investigations (which neglected thermal creep), the temperature distribution in the ampoule was assumed one dimensional and linear in the axial direction. An iterative scheme was developed to solve the continuity, momentum and species equations and ideal-gas equation of state for the pressure, density, mass fraction and velocity fields in the ampoule. The ampoule that was modelled in the numerical study had an aspect ratio of 5 and contained a nutrient with a molecular mass of 254 g/mole and a carrier with a molecular mass of 2 g/mole. The total pressure in the ampoule was 100 torr and the partial pressure of the nutrient at the source

and crystal ends was 80 and 50 torr, respectively. A parametric investigation was made of the effect of the relative temperature difference $\Delta T/T_S$ across the source and crystal interfaces and the Schmidt number $Sc = \nu/D_{AB}$ on the creep-induced flows and crystal growth rates.

As expected, thermal creep establishes a recirculation pattern in the ampoule. The fluid at the side walls is driven towards the high-temperature source, and returns to the crystal along the ampoule centerline. Although the creep-generated velocities could be well in excess of those predicted without creep, the effect of creep on total mass transfer rates appears to be minimal for all but the largest realistic values of $\Delta T/T_S$ and Sc . For example, a $\Delta T/T_S$ of 0.2 and a Sc of 10 produced centerline velocities over 170% greater than predicted without creep, yet the total mass transfer rates were only 0.3% greater. Higher values of Sc , on the other hand, resulted in significantly larger mass transfer rates – on the order of 70% greater for $Sc = 100$.

Because the validity of a linear temperature distribution is questionable in the presence of strong creep-generated flows, the numerical model has been recently extended to include the energy equation with adiabatic or fixed-temperature ampoule side walls. In addition, transient flows are now being simulated, as are cartesian as well as cylindrical ampoules. Results from this model indicate that a more apparent effect of thermal creep recirculation is a decrease in the uniformity of mass flux rates across the crystal interface. For example, the conditions of $\Delta T/T_S = 0.2$ and $Sc = 10$ resulted in a 5% relative change in crystal growth rates from the centerline to the wall, whereas the nonuniformity in growth rates that was calculated for the same conditions except without creep was negligible.

In practice, the ampoule wall temperature distribution can be highly nonlinear in axial position. This could have a profound effect on thermal creep, and is the next topic to be examined in this study. Future work also includes consideration of the previously neglected Burnett contributions of thermal stress to the fluid stress tensor. In addition, fluid property variation as a function of local temperature and vapor concentration will be included. The observed variation in crystal growth rate across the crystal face can also have implications regarding the stability of the crystal interface. Simulations of “non-smooth” crystal interfaces will be performed, and deposition rates will be examined to determine if surface perturbations will grow or diminish. Transient effects, such as start up times and time variable gravitational acceleration will also be examined.

References

1. Walker, D.G., Mackowski, D.W., and Knight, R.W., “The Effects of Thermal Creep on Physical Vapor Transport Under Microgravity Conditions,” AIAA 32nd Aerospace Sciences Meeting and Exhibit, 10–13 January 1994, Reno, NV, paper 94–0567.

Research Summary

The Effect of Gravity on Natural Convection and Crystal Growth

PI: Dr. Graham de Vahl Davis (Dr. E. Leonardi and Students, University of New South Wales, Australia)

CoI: Henry C. de Groh III (from NASA Lewis, Dr. M. Yao, Ohio Aerospace Inst.)

Starting date: Jan. 1993. Period covered by this summary: Jan. 1993 to April 1994. For the Microgravity Materials Science Conference, May, 1994.

Objectives

- 1) To measure experimentally natural convection during Bridgman growth at varying gravity-driven levels and to quantitatively determine how this convection affects parameters of critical importance to the crystal grower such as interface shape, and radial and longitudinal segregation.
- 2) To produce an accessible, experimentally verified numerical code capable of accurately determining levels of convection in real systems at varying gravity levels and directions, and the effects of this convection on the solidification process.
- 3) To supply and supplement numerical modeling efforts for the MEPHISTO II flight experiment of Dr. R. Abbaschian.

Application to Space Processing and Need

The major goal of many space experiments in solidification is to determine how convection influences various phenomena such as undercooling at the solid/liquid interface, redistribution of solute, and crystal quality. However, in most flight experiments, as in the MEPHISTO experiments which are being done using an opaque alloy of Bi-Sn, no measurements of convection are possible. Our research will yield experimentally verified codes capable of calculating amounts of convection present in the melt at 1-g horizontal, vertical, and various intermediate angles and in low-g with various residual gravity values, angles and frequencies. Thus it is hoped that current flight experiments, as well as future flight experiments, will benefit from this research. Two codes are under development: a modified version of the commercial finite element code FIDAP (due to M. Yao), and a finite difference code (due to G. de Vahl Davis, E. Leonardi and students). Both may be available to MSAD investigators through use of the Computational Materials Laboratory (NASA Lewis, Arnon Chait) and/or collaboration with the PI. The models will complement the scaling, analytical modeling and parametric experimental studies of others (Coriell, Favier, Thevenard and Camel) and will be used to check the validity, extension and generalization of scaling laws. We are using the transparent metal analog succinonitrile, which allows direct analysis of convection and interface shape.

Progress to date

An overview follows, with details found in our papers listed below.

Solidification Experiments

Experimental studies of succinonitrile during solidification, melting and no-growth conditions using a horizontal Bridgman furnace and square glass ampoules have been conducted. For use as

input boundary conditions to the numerical codes, thermal profiles inside and on the outside of the ampoule were measured. The shapes of the s/l interface in various 2-D planes were quantitatively determined. Though interfaces were non-dendritic and non-cellular, they were not "flat," but were highly curved and symmetric in the vertical, longitudinal plane. The shape of the interfaces were dominated by the primary longitudinal flow cell characteristic of shallow cavity flow in horizontal Bridgman; this flow cell was driven by the imposed furnace temperature gradient and caused a "radial" thermal gradient such that the upper half of the ampoule was hotter than the bottom half. These data^{3,4} will be used to examine the numerical models.^{5,8} Presently underway is an effort to measure fluid flow velocities and interface shape and convective modes at various ampoule angles between vertical and horizontal.

Numerical Modeling

The results of the numerical codes have been compared to the experiments in succinonitrile and excellent agreement has been achieved. The codes have been used to predict interface shape, thermal fields and fluid flow velocities during horizontal Bridgman no-growth, and solidification conditions in 2-D and 3-D. The segregated solution approach has enabled fine mesh 3-D solidification simulations, using FIDAP, to be run on a work station. The front tracking technique and solute concentration have been incorporated into the finite element model. In contrast to the formerly used enthalpy-type method, the front tracking technique involves a deforming spatial grid and is able to model phase changes with sharp interfaces. These new efforts have greatly enhanced the capability of our numerical simulations. Using the front tracking method, a 2-D simulation of the MEPHISTO II vertical 1-g and space experiments has been done;⁶ it was found at $g < 10^{-4}$ earth gravity, solidification was diffusion controlled. 3-D finite difference solution methods using body-fitted coordinates have allowed an accurate representation of the interface shape, position and growth to be obtained, together with detailed results for the flow pattern and temperature distribution. Other low-g simulations⁸ are underway and future efforts will include non-steady gravities (g-jitter) and with g at various angles to the ampoule axis, as is expected in space.

Papers due to this work:

- 1) "A Numerical and Experimental Study of Natural Convection and Interface Shape in Crystal Growth," by G.H. Yeoh, G. de Vahl Davis, E. Leonardi, H.C. de Groh III, and M. Yao, in proceeding of the First International Conference on Transport Phenomena in Processing, S.I. Güçeri editor, 1993, pp. 98-109.
- 2) "Segregated Solution in 3-D Modeling of Crystal Growth," M. Yao and H.C. de Groh III, LEW-15672, NASA Tech Brief Vol. 17, No. 11, 1993.
- 3) "Three-Dimensional Finite Element Method Simulation of Bridgman Crystal Growth and Comparison with Experiments," by M. Yao and H.C. de Groh III, Numerical Heat Transfer, Part A, Vol. 24, 1993, pp.393-412.
- 4) "Interface Shape and Convection during Melting and Solidification of Succinonitrile," by H.C. de Groh III and Tiffany Lindstrom, in press, NASA Technical Memorandum 107724, 1994.
- 5) "Numerical and Experimental Study of Transport Phenomena in Directional Solidification of Succinonitrile," by H.C. de Groh III and M. Yao, submitted for publication in the proceedings of the 1994 ASME Winter Annual Meeting.
- 6) "Numerical Modeling of Bridgman Growth in Space with MEPHISTO," by M. Yao and H.C. de Groh III, submitted to the 1994 ASME Winter Annual Meeting, Chicago IL, Nov. 6-11, 1994.
- 7) "On Residual Acceleration During Space Experiments," by H.C. de Groh III and E.S. Nelson, submitted to the 1994 ASME Winter Annual Meeting, Chicago IL, Nov. 6-11, 1994.
- 8) "Bridgman Crystal Growth in Reduced Gravity," by H.C. de Groh III, G. de Vahl Davis, E. Leonardi and M. Yao, in preparation for the Symposium on Microgravity Sciences and Processes, 45th IAF Congress, Jerusalem, Israel, Oct. 9-14, 1994, authors in alphabetical order.

GROWTH OF SOLID SOLUTION SINGLE CRYSTALS

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Co-Investigators: Dr. Frank R. Szofran
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NASA/George C. Marshall Space Flight Center

The objective of the study is to establish the effects of processing semiconducting, solid solution, single crystals in a microgravity environment on the metallurgical, compositional, electrical, and optical characteristics of the crystals. The alloy system being investigated is the solid solution semiconductor $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, with x-values appropriate for infrared detector applications in the 8 to 14 μm wavelength region. Both melt and Te-solvent growth are being performed. The study consists of an extensive ground-based experimental and theoretical research effort followed by flight experimentation where appropriate. The objectives of the ground-based research effort are to : (1) obtain the experimental data and perform the analyses required to define the optimum growth parameters for the flight samples, (2) quantitatively establish the characteristics of the alloy crystals grown in a 1-g environment as a basis for subsequent comparative evaluations of the alloy crystals grown in microgravity, and (3) develop theoretical and analytical methods required for such evaluations. The ground-based portion of the investigation also includes the evaluation of the relative effectiveness of stabilizing techniques, such as applied magnetic fields, for suppressing convective flow during the melt growth of the crystals.

The difficulty of growing bulk crystals, with both radial and axial homogeneity of significant lengths in Earth's gravity is well documented. Because the HgTe-rich component rejected during solidification is more dense, the vertical Bridgman-Stockbarger growth process would appear to be both gravitationally and thermally stable against convection, but this is not generally true. Due to the peculiar relationships between the thermal conductivities of the melt, solid, and ampule, it is practically impossible to completely avoid radial temperature gradients in the growth region. In general, the presence of radial temperature gradients near the growth region will cause a curvature in the solid-liquid interface which need be neither an isothermal nor an isoconcentrational surface. Furthermore, the growth of high quality crystals usually requires a slightly convex growth interface as viewed from the melt. Under the influence of stable growth conditions, such interface geometries readily lead to lateral alloy segregation because of the tendency of the more dense HgTe-rich liquid to settle at the portions of the surface having the lowest gravitational potential. Because the alloy solidus temperature decreases with increased HgTe content, the interface temperature will be lowered in this region, causing the interface curvature to increase. Although lateral diffusion will tend to drive the interfacial melt compositions to some equilibrium values, most ground-based melt-growth experiments show large radial compositional variations that are probably a direct consequence of such an interfacial fluid flow phenomenon. In low gravity it is expected that the highly desired slightly convex growth surfaces will be easier to maintain because of the reduced tendency for stratification of the denser (HgTe rich) fluid component. At the same time, the near-elimination of radial temperature gradient-driven convection is expected to provide for a better control of the lateral compositional distribution in the melts. It is thus expected that by growing under the influence of low-gravity conditions ($g \leq 10^{-6}g_0$), crystals with significantly improved crystallinity and compositional homogeneity can be prepared as compared to the best crystals that can be produced on Earth. It is also reasonable to expect that careful characterization of both the space- and ground-grown materials will lead to better insights into the peculiarities of the various growth mechanisms that will permit improvements in Earth-based processing of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and other compound semiconductor alloy systems.

It is believed that CdTe, $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, etc. probably possess extremely small yield strengths near their growth temperatures. If this is the case, the high dislocation density ($\sim 10^5 \text{ cm}^{-2}$) usually seen in these crystals could be due at least in part, to stresses induced by the samples own weight, that is, self-

induced stresses. Therefore, a second goal of these experiments is to assess the validity of this hypothesis.

Over the past several years, a detailed evaluation has been performed on the effects of growth parameters on the axial and radial compositional uniformity, defect density, and optical properties in directionally solidified $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and other similar compounds and pseudo-binary alloys. A series of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloy ingots ($0 < x \leq 0.6$) has been grown from pseudobinary melts by a vertical Bridgman-Stockbarger method using a wide range of growth rates and thermal conditions. Several of the experiments were performed in transverse and axial magnetic fields of up to 5T. Precision measurements were performed on the ingots to establish compositional distributions and defect density distributions for the ingots. Correlation between growth rates and thermal conditions and growth interface shapes have been established for the alloy system. To assist the interpretation of the results and the selection of optimum in-flight growth parameters, the pseudobinary phase diagram ($0 \leq x \leq 1$), liquid and thermal diffusivities ($0 \leq x \leq 0.3$), melt viscosity, and the specific volumes as a function of temperature ($0 \leq x \leq 0.15$) have been measured. From these measurements and other available data, the heat capacity, enthalpy of mixing, and the thermal conductivity of pseudobinary melts have been calculated using a regular associated solution model for the liquid phase. A one-dimensional diffusion model that treats the variation of the interface temperature, interface segregation coefficient, and growth velocity has been used to establish effective diffusion constants for the alloy system. Theoretical models have been developed for the temperature distribution and the axial and radial compositional redistribution during directional solidification of the alloys. These were used along with the experimental results to select the parameters for the first flight experiment flown on the Second United States Microgravity Payload (USMP-2) mission. A microscopic model for the calculation of point-defect energies, charge-carrier concentrations, Fermi energy, and conduction-electron mobility as functions of x , temperature, and both ionized and neutral defect densities has been developed. For selected samples, measurements were performed of electron concentration and mobility from 10-300K. The experimental data were in reasonably good agreement with theory and were successfully analyzed to obtain donor and acceptor concentrations for various processing conditions.

A five zone Bridgman-Stockbarger type "Advanced Automatic Direction Solidification Furnace (AADSf)" has been designed and developed for the flight portion of the investigation. The AADSf was successfully flown on the USMP-2 mission in March 1994 during which a 15 cm long and 0.8 cm diameter $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ alloy crystal was grown under precisely controlled residual acceleration conditions over a period of approximately 11 days. Preliminary x-radiographs of the crystal indicate that the growth was successful. Characterization of the crystal is in progress.

Compound Semiconductor Growth in Low g Environment

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Objective:

The objective of this flight program is to determine the effects of gravity driven convection on the growth conditions and crystal properties of the compound semiconductor alloy, lead tin telluride which is a substitutional alloy that is miscible over the entire compositional range. The electronic properties of this material are dependent on the ratio of the two components and consequently, the uniformity of an array of devices is dependent on good compositional control. Lead tin telluride is amenable to study for it is easily compounded; it has a relatively low vapor pressure; and there is existing, though limited, literature on its growth and properties.

This material was chosen for microgravity research for a number of reasons. Lead tin telluride is not only a useful semiconductor material which has been used for construction of Infrared detectors and tunable diode lasers. It also has a similar phase diagram to other compound semiconductors of interest such as mercury cadmium telluride and mercury zinc telluride.

Relevance for Microgravity:

Lead tin telluride is also interesting from a purely scientific point of view in that it is both solutally and thermally unstable. Both the temperature gradients and the compositional changes in the liquid near the melt/solid interface produce density gradients which, in turn, produce driving forces for convection when coupled with gravity.

Earth based growth of lead tin telluride has only produced inhomogeneous crystals that are a result of strong convective forces in the liquid during growth. The temperature gradients are required for growth and the solutal changes at the interface are a

fundamental property of the material system. However, for convection to occur these gradients must be coupled to a gravitational field. Growth in low Earth orbit offers a unique and fascinating opportunity to study the effect of convection on this class of materials. The resultant gravitational force is not zero in low Earth orbit hence convection is not completely eliminated but the fluid velocity, due to convection, will be greatly reduced.

Two flights are planned in the Advanced Automated Directional Solidification Furnace (AADSf). The primary objective of both flights is to study the effect of gravity reduction, hence convection reduction, on the growth of lead tin telluride. In one experiment the growth rate of the crystal will be changed in steps to test the effect of varying the relative speed of the interface movement and the fluid velocity. In the other experiment the Space Shuttle will be rotated to vary the relative orientation of the gravity vector and the crystal growth axis. Both sets of experiments are expected to affect the compositional homogeneity of the crystal.

Progress to Date:

This year's effort concentrated on finalizing the AADSf furnace configuration and calibration. Lead tin telluride has been grown in the flight configuration. The newly designed calibration cartridge has been used for extensive characterization of the AADSf furnace. Doped germanium samples, with interface demarcation, have been grown in the prototype AADSf for comparison to the calibration data. Numerical modeling of the furnace and samples is presently underway for subsequent extrapolation to modeling of lead tin telluride in the furnace.

A cartridge with a miniature, internal, pressure gauge was designed and tested in furnaces both at Langley and Marshall. These tests not only measured the pressure as a function of set point temperatures (yes, the gas law still applies) over the different thermal gradients but also measured the integrity of the cartridge seals and the rigidity of the cartridge as a function of temperature and differential pressure.

We have also continued with compatibility tests between the lead tin telluride and potential cartridge materials. The Inconel cartridge does not contain molten lead tin telluride but tests with WC-103 indicate that this material is impervious to the molten charge for at least the length of time of a typical growth run.

**ORBITAL PROCESSING
OF
HIGH-QUALITY CdTe COMPOUND SEMICONDUCTORS**

**D. J. Larson, Jr.
Principal Investigator**

**J. I. D. Alexander
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Co-Investigators**

SUMMARY

The Orbital Processing of High-Quality CdTe Compound Semiconductors program was initiated to investigate quantitatively the influences of gravitationally dependent phenomena on the growth and quality of compound semiconductors. The objective was to improve crystal quality (structural and compositional) and to better understand and control the variables within the crystal growth production process. The empirical effort entailed the development of a one-g experiment baseline for quantitative comparison with the microgravity (μ -g) results. This empirical effort was supported by the development of high-fidelity process models of heat transfer, fluid flow and solute redistribution, and thermo-mechanical stress occurring in the furnace, safety cartridge, ampoule, and crystal throughout the melting, seeding, crystal growth, and post-solidification processing.

CdZnTe crystals were grown in one-g and in μ -g for comparative analysis. The two μ -g crystals were grown in the Crystal Growth Furnace during the First United States Microgravity Laboratory Mission (USML-1). It was anticipated that the μ -g environment would damp gravitationally dependent convection, improving chemical homogeneity. More importantly, for this investigation, it was anticipated that the near-absence of hydrostatic pressure would reduce the hoop stresses experienced by the growing and cooling crystal, thus reducing the defect density within the flight samples. The one-g and μ -g samples were thus analyzed for chemical homogeneity, opto-electronic performance (Infrared

transmission), and structural perfection.

Macrosegregation was predicted to be low in one-g and μ -g, using scaling analysis. This was confirmed experimentally, with nearly diffusion controlled growth achieved even in the partial mixing regime terrestrially. Radial segregation was monitored in the flight samples and was found to vary with fraction solidified, but was disturbed due to the asymmetric gravitational and thermal fields experienced by the flight samples from USML-1. Thermally symmetric fields will be arranged for the follow-up flight experiment on USML-2 to improve this measurement.

FTIR transmission of both ground and flight materials was measured to be close to theoretical; 63% versus 66% (theoretical). This suggested that both the ground and flight materials were close to the stoichiometric composition. Infrared microscopy and x-ray measurements confirmed that the principal precipitates were Te and their size (1-10 μ m) and density suggested that the both primary flight and ground base samples experienced similar cooling rates and were close to stoichiometry.

The flight samples, however, were found to be much higher in structural perfection than the ground samples produced in the same furnace under identical growth conditions except for the gravitational level. Rocking curve widths were found to be substantially reduced, from 20/35 arc-seconds (one-g) to 9/15 arc-seconds (μ -g) for the best regions of the crystals. The value of 9 arc seconds equals the best reported terrestrially for this material. Morphologically, the ground samples were found to have a fully developed mosaic structure consisting of subgrains and large regions of cross-slip, whereas the flight samples exhibited discrete dislocations and no mosaic substructure or cross-slip was evident. The defect density was reduced from 50,000-100,000 (one-g) to 500-3000 EPD (μ -g). This, too, is the lowest reported.

The thermo-mechanical model suggested that the low dislocation density was due to the near-absence of hydrostatic pressure in μ -g which allowed the melt to solidify with minimum wall contact, reducing the stress transmitted to the crystal during growth and post-solidification cooling. Further, the highest quality material was predicted to be on the periphery of the boule, unlike the terrestrial samples where the best material is at the core, and this was confirmed microstructurally.

Our follow-up experiment on USML-2 will process the flight sample in a thermally symmetric environment, with full wall contact. This will complete the comparative matrix and test further the validity of the models.

CRYSTAL GROWTH OF SELECTED II-VI SEMICONDUCTING ALLOYS BY DIRECTIONAL SOLIDIFICATION

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This research study is investigating the effects of a microgravity environment during the crystal growth of selected II-VI semiconducting alloys on their compositional, metallurgical, electrical and optical properties. The on-going work includes both Bridgman-Stockbarger and solvent growth methods, as well as growth in a magnetic field. The materials investigated are II-VI ternary semiconducting compounds such as $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$, and $\text{Hg}_{1-x}\text{Zn}_x\text{Se}$ ($0 \leq x \leq 1$), with particular emphasis on x-values appropriate for infrared detection and imaging in the 5 to 30 μm wavelength region. Wide separation between the liquidus and solidus of the phase diagrams with consequent segregation during solidification and problems associated with the high volatility of one of the components (Hg), make the preparation of homogeneous, high-quality, bulk crystals of the alloys nearly an impossible task in a gravitational environment.

The three-fold objective of the on-going investigation is as follows:

1. to determine the relative contributions of gravitationally-driven fluid flows to the compositional redistribution observed during the unidirectional crystal growth of selected solid solution semiconducting alloys having large separation between the liquidus and solidus of the constitutional phase diagram,
2. to ascertain the potential role of irregular fluid flows and hydrostatic pressure effects in generation of extended crystal defects and second-phase inclusions in the crystals, and
3. to obtain a limited amount of "high-quality" materials needed for bulk crystal property characterizations and for the fabrication of various device structures needed to establish ultimate material performance limits.

The flight portion of the study is being accomplished by performing growth experiments using the Crystal Growth Furnace (CGF) manifested to fly on various Spacelab missions. The investigation complements the experiments being done on the crystal growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ using the Advanced Automatic Directional Solidification Furnace (AADSDF) flight instrument. The main emphasis of the study involves the $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ and $\text{Hg}_{1-x}\text{Zn}_x\text{Se}$ alloys. The investigation consists of an extensive ground-based study followed by flight experimentation and involves both experimental and theoretical work. Just as for the AADSDF-related studies, both melt and solvent growth methods are being pursued, with the melt growth being the primary emphasis of the initial flight experiments. The combination of the two studies provides the basis for the evaluation of the influence of alloy property variations on the relative importance of various gravity- and non-gravity-related effects. Several alloy properties including the effective diffusion coefficient, segregation coefficient, thermal conductivity, microhardness, etc. are

known to vary substantially with composition and from alloy system to alloy system. For example, the "effective" mass diffusion coefficients deduced from directional solidification compositional redistribution data differ by over a factor of 20, with that of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ being the largest and $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ being the smallest. These variations will cause non-gravity-related effects to be more significant in some cases than in others.

A series of HgZnTe crystal ingots has been grown from pseudobinary melts by Bridgman-Stockbarger type directional solidification using the CGF Ground Control Experiment Laboratory (GCEL) furnace, as well as MSFC heat pipe furnaces. Several ZnTe crystals were also grown using a Te -solvent zone growth method. Various thermal boundary conditions and growth rates were employed and several of the ingots were rapidly quenched during the steady-state portion of growth to establish correlation between thermal conditions and melt/solid interface shapes. These experiments also indicated that the ingots can be successfully quenched and back melted to allow a rapid return to steady-state growth. The fitting of the measured crystal compositional distributions to appropriate theoretical models was used to obtain an estimate of the effective HgTe-ZnTe liquid diffusion coefficients. To assist the modeling of the pertinent heat and mass transport processes, selected portions of the pseudobinary phase diagram, thermal diffusivity and melt viscosity have been measured. Growth experiments for an $\text{Hg}_{0.84}\text{Zn}_{0.16}\text{Te}$ alloy crystal were also performed that showed significant fluid flow effects on the crystal compositional distributions.

A ground preprocessed and quenched sample was successfully back-melted and partially regrown in the CGF instrument during the first United States Microgravity Laboratory (USML-1) mission. The meltback interface was within 0.5 mm of the desired value. Because of the loss of power to the CGF, the experiment was terminated after approximately 39 hours into the growth period. About 5.7 mm of sample had been grown at that point.

Surface photomicrographs of the removed sample clearly showed significant topographical differences between the space- and ground-grown portions. Compositional measurements along the sample axis indicated that the desired steady-state growth for the axial composition was reached at about 3 mm into the growth. An X-ray diffraction and SEM survey of the sample showed that both the ground- and flight-portions of the ingot contained only a few grains, i.e., were nearly single crystals, and the crystallographic orientation was maintained following back-melting and space growth. The interface shape, radial compositional variations, and the quenched-in dendretic structures of the flight sample all have shown an asymmetric behavior. The compositional data strongly suggest that the most likely cause was unanticipated transverse residual accelerations.

Program Title:

The Study of Dopant Segregation During the Growth of GaAs in Microgravity

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Viable Systems

NASA Contract Number: NAS8-397

Program Initiation: 5/92

Program Objectives:

The scientific objectives of this program are to develop an understanding of the axial and radial dopant distribution (segregation behavior) of the selenium dopant during the crystal growth of gallium arsenide (GaAs). This program will investigate gravitational and thermal techniques for obtaining complete axial and radial dopant uniformity in the grown crystal. The thermal techniques include using a five zone modified Bridgman-Stockbarger furnace to obtain a flat interface shape and steady-state growth rate. The gravitation techniques include growth in the microgravity environment afforded by the Crystal Growth Furnace (CGF) in the second United States Microgravity Laboratory (USML-2).

The Role of Gravitational Phenomena

The reduced effective gravitational accelerations in a microgravity environment can reduce or eliminate the driving force for buoyancy driven convection. This can be understood by examining the coupled heat, mass and momentum transport equations shown below:

the continuity equation:
$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \vec{U}$$
 Eq. 1

the momentum equation:
$$\frac{\partial}{\partial t} (\rho \vec{U}) = -\nabla \cdot \rho \vec{U} \vec{U} - \nabla \cdot \vec{\tau} - \nabla F_s + \vec{F}_b$$
 Eq. 2

the energy equation:
$$\frac{\partial T}{\partial t} = -\vec{U} \cdot \nabla T + \nabla \cdot (\alpha \nabla T)$$
 Eq. 3

the mass equation:
$$\frac{\partial C}{\partial t} = -\vec{U} \cdot \nabla C + \nabla \cdot (D \nabla C)$$
 Eq. 4

The body force in the momentum equation is due to the temperature dependence of the density.

the body forces:

$$\vec{F}_b = \rho(T) \vec{g} \quad \text{Eq. 5}$$

On earth, these transport equations are completely coupled. That is, the temperature dependence of the density (Eq. 5) drives the fluid flow U (Eq. 2). The fluid flow U couples to the thermal transport and the mass transport in Eq. 3 and Eq. 4 as a convective contribution.

Many numerical simulations, using the fundamental transport equations listed above and assuming various simplifying assumptions, have been conducted on the Bridgman-Stockbarger crystal growth process. An example of these is shown in Fig. 1 from the work of Brown and his co-workers at MIT.

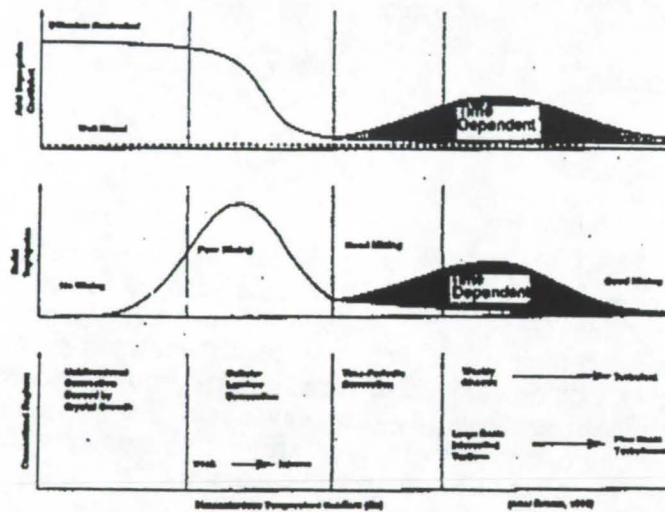


Fig. 1. Predicted radial and axial segregation behavior as a function of convection.

In Fig. 1, it can be seen that, as the level of convection is reduced (i.e. the gravitational acceleration, g , in Eq. 5 is reduced), the axial segregation quickly approaches that of diffusion controlled growth. The radial segregation however, tends to increase and then finally decrease to a level determined by the interface curvature. Thus, if diffusion controlled growth is achieved in microgravity, and the interface shape is severely curved, then the radial segregation can be larger than that of earth based processing.

Thus it is predicted that the microgravity environment is necessary to achieve diffusion controlled growth and therefore a uniform dopant distribution in the axial direction and in addition, control of the interface shape is necessary for a uniform dopant distribution in the radial direction.

Significant Results to Date and Future Plans:

This program required the significant development efforts for: a flight qualified interface demarcation unit capable of delivering a current pulse of the amplitude, duration and pattern desired; an ampoule which allowed electrical contact to the solid and liquid GaAs during growth; a cartridge to safely contain the GaAs, allow pressure balance on the ampoule and provide electrical connection to the pulsing unit. These efforts culminated in the first operation test of the sample-ampoule-cartridge-assembly (SACA), the results of which are currently being evaluated.

VAPOR TRANSPORT CRYSTAL GROWTH OF MERCURY-CADMIUM-TELLURIDE IN MICROGRAVITY USML-2 EXPERIMENTS

NASA Contract NAS8-39723

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This project is concerned with the investigation of the transient behavior of the growth of thin $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ layers on (100) CdTe substrates by chemical vapor transport in closed ampoules under normal and microgravity conditions.

The results of our earlier USML-1 experiments of the vapor phase epitaxial growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ on CdTe substrates demonstrate significant improvements in the chemical and structural microhomogeneity of space-grown layers relative to ground samples. In particular, the surface morphology, the compositional uniformity, and the crystallographic perfection of the epitaxial layers grown in space are quantitatively better than those of the ground-control specimens. An important observation of the USML-1 analysis are the considerable differences between the detailed microstructures of the epilayer-substrate growth interface for the flight and ground samples. The growth interfaces of the ground samples reveal very high dislocation densities leading to etch pit overlapping. Those of the flight samples have a much lower etch pit density, indicating a nearly "seamless" transition from the substrate to the epitaxial layer. The above observations of the growth interface structure provide strong experimental evidence for the effects of residual convection (under vertical, stabilizing conditions) on the epitaxial deposition and growth processes at the very beginning of this process.

The microgravity environment provides a unique opportunity to investigate the interactions of mass flow with the growth processes from the onset of deposition, and to follow the propagation of "birth defects" during subsequent growth. For this purpose, epitaxial growth experiments of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ on CdTe substrates using HgI_2 as a transport agent in closed fused silica ampoules are performed. The transient studies of the USML-2 experiments are concerned with an in depth investigation of the growth of thin layers of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ on CdTe substrates. Such experiments have never been performed in microgravity. The results expected from these investigations are both fundamental in nature and of technological significance.

The objectives of this investigation are to observe basic growth phenomena during the critical transient time, t_c , required for the transition from 3-dimensional island to 2-dimensional layer growth. The above discussed observations strongly suggest that convective interference on ground influences the critical transient time. This "interference" leads to related effects on the chemical and structural microhomogeneity of the epitaxial layer. Convective mass flow on ground may influence the initial nucleation on a microscopic scale. In order to verify this proposal, the following specific growth properties are to be measured on ground and in microgravity: (a) The critical transient time, t_c , to provide a measure of convective interferences on ground. (b) The time (thickness) dependence of the local and spatial layer composition uniformity. (c) The time dependence of the island/layer growth rate. (d) The substrate-layer interface and layer morphology as a function of growth time (thickness). From a quantitative comparison of the analyses of the ground and space experiments, the effects of microgravity on the initial deposition and growth processes can be ascertained. These experiments provide basic scientific information for crystal growth, they establish practical limits for optimum growth conditions, and, thus, they are useful for the improvement of crystal growth on ground.

The results of ground-based experiments to date are consistent with the above discussion. The critical transient time and the island-layer morphology support the effects of convective mass flow on the initial deposition and growth processes. The time dependence of the composition and of the growth rate of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ layers are currently being analyzed in terms of the physico-chemical properties of this growth system. Continued ground-based studies are designed to quantitatively determine convective effects on the above crystal growth properties, to differentiate them from those of other parameters, and to optimize the microgravity experiments. Under these conditions, the detailed history of growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ layers on CdTe substrates under normal and microgravity conditions can be established.

VAPOR CRYSTAL GROWTH OF MERCURIC IODIDE

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A single crystal of Mercuric Iodide (HgI_2) has been grown during five days of the flight of IML-1. After return to earth, the overall structural quality of the crystal was determined by means of gamma ray diffraction rocking curves. The crystal was then removed from the growth ampoule and slices were cut from it. Radiation detector devices were manufactured from these slices by applying contacts. This allowed for the measurement of the electronic properties of the material in terms of charge carrier mobilities and mobility-lifetime products. In addition, x-ray topography was performed on a slice of the material to further characterize the structural quality of the lattice and the nature of the lattice defects.

The same measurements were made on crystals grown on the ground from the same material, so that the results could be compared.

Objectives of the Investigation

1. Construct a crystal growth system which can operate in microgravity and can establish and maintain the same operating parameters as are used on the ground.
2. Perform a crystal growth experiment in space with optimized experimental parameters as determined by the crew member in consultation with the ground crew.
3. Determine the quality of the space-grown crystal (structural, electronic) and compare with ground-based crystals.

4. Compare morphological stability and transport rates during growth. Formulate a qualitative explanation.

Benefits of Microgravity

The microgravity is needed to eliminate convection in the growth ampoule so that diffusion-controlled vapor transport can be obtained. In addition, hydrostatic forces on the crystal caused by its own weight are avoided. Both factors are expected to influence the crystalline structure, and thereby the electronic properties.

Results

The gamma ray rocking curves showed that the space crystal consisted of two domains with an angular deviation of 0.06 degrees between the domains. By comparison, the most regular of the ground-based crystals consisted of three domains with an angular deviation of 0.2 degrees. Measurements of the mobilities of the electrons and holes showed that the values for the space crystal are approximately twice as large as for the ground-based crystals. The mobility-lifetime product for the holes, the most critical factor for device performance, was approximately ten times higher for the space crystal. The x-ray topography showed that the angular deviations in the space crystal were approximately 15 times smaller than for the best earth-grown crystal.

Future Plans

The results of the SL-3 and IML-1 experiments confirmed that the Vapor Crystal Growth System is able to grow crystals reliably and with consistent results. The next step would be to instrument the growth ampoule extensively so that a detailed temperature profile of the growth ampoule can be obtained, and possibly the temperature of the surface of the growing crystal can be measured. This will provide adequate data for detailed fluid dynamics calculations.

David H. Matthiesen

Diffusion Processes in Molten Semiconductors

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"DIFFUSION, VISCOSITY AND CRYSTAL GROWTH IN MICROGRAVITY"

NASA Grant NAG-8-960

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I. OBJECTIVES

The overall objectives of this project are:

1. Experimental studies of the diffusion coefficients and viscosity of triglycinesulfate (TGS), KDP and other compounds of interest to microgravity crystal growth, in supersaturated solutions as a function of solution concentration, solution 'age' and solution 'history'.
2. Development of a theoretical model of diffusion and viscosity in the metastable state.
3. Develop a model of crystal growth from solution including nonlinear time dependent diffusion and viscosity effects.
4. Employ the model with and without buoyancy driven convective flows to predict results of earth and microgravity crystal growth experiments and to compare these results to experimental results.
5. Develop a computer simulation of the crystal growth process which will allow simulation of microgravity crystal growth including the effects mentioned above.

II. RELATIONSHIP OF INVESTIGATION TO MICROGRAVITY RESEARCH

Crystal growth from solution is a complex process in which diffusional mass transfer and free convective mass transfer (due to density gradients) are important. Several investigators have demonstrated the existence of convective flow currents around the crystal-liquid interface. These currents (often called a convective "plume") are one reason for the difficulty in growing large good quality crystals at a reasonable rate in many systems. Crystal growth in a microgravity environment eliminates the convective mass transfer problem. The dominant mass transfer mechanism, therefore, become diffusional mass transfer. An accurate understanding of diffusion coefficient behavior at the conditions at which the crystallization takes places is, therefore, a crucial aspect of crystal growth in space. This can be illustrated by the work of Yoo et al (1) who modelled the crystal growth of TGS and compared these results to those obtained in a Spacelab 3 experiment. They concluded that the growth was 90% diffusion controlled. In addition, they compared calculated

concentration profiles around the TGS crystal with those measured during the experiment. They could not obtain good agreement using a diffusion coefficient measured at saturation.

The growth of a crystal from solution requires the solution be supersaturated. Diffusion coefficients in supersaturated solutions however are rarely known. Myerson and coworkers (2) have shown that diffusion coefficients are a strong declining function of concentration in the supersaturated region and a weak function of solution 'age'. They have also shown similar but weaker effects on concentration and 'age' of solution viscosity. Since diffusional mass transfer is the dominant mechanism for crystal growth in microgravity, data of this kind is required for the proper design and analysis of microgravity crystal growth experiments.

III. RESULTS TO DATE

Experimental studies were conducted in support of objective 1. These measurements included diffusivity and viscosity measurement of ADP, KDP and TGS in undersaturated, saturated and supersaturated solutions and measurement of the effect of solution 'age' on diffusivity in these systems. All diffusion measurements were done employing a Gouy interferometer.

A Spherical Void Electrodynamic Levitator Trap (SVELT) was employed to measure the activity and activity coefficients in highly supersaturated solutions of TGS, KDP and ADP. This data was obtained far into the metastable region approaching the spinodal curve.

Model development in support of objectives 2 and 3 has begun and resulted in the determination of a general relationship between viscosity and density at saturation during crystal growth.

Future work in this project will involve additional experimental studies of concentration and 'age' effects on diffusion and viscosity in supersaturated solutions and the development of a crystal growth model which takes these effects into account along with variable viscosity effects.

1. Yoo, H.D., et al. J. Cryst. Growth, 92, 101 (1988).
2. Myerson, et al., AIChE J. 28, 772 (1982), 30, 820 (1984), 32, 1567 (1986), 33, 697 (1987), J. Cryst. Growth, 99, 1048 (1990) 110, 26 (1991).

Melt Stabilization of PbSnTe in a Magnetic Field

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NASA Langely Research Center

Co-Investigators: William J. Debnam
NASA Langely Research Center

Frank R. Szofran
NASA Marshall Space Flight Center

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Objective:

The primary scientific objective of this study is to clarify the role of gravity on physical phenomena during the growth of the alloy compound semiconductor PbSnTe (LTT). In particular, this research is concerned with the study of the effects of the gravitational body force on convection in the LTT melt. This objective will be achieved via a systematic examination of gravitationally-driven phenomena using both earth and reduced gravity levels, and by using magnetohydrodynamic (MHD) damping at both gravity levels. LTT serves as a representative material for a class of semiconductors used for detection and lasing applications for which the compositional homogeneity, as determined by the double-diffusive convection in the melt, is of paramount importance. The experimental program will be integrated with a comprehensive numerical simulation program to bring together a complete picture of the double-diffusive convection in the melt and its influence on the growing crystal.

Relevance for Microgravity:

Gravitationally-driven convection in the LTT melt can be classified as a double diffusive convection. For the pseudo-binary alloy of LTT, increases in temperature and in composition both decrease the melt density. Depending on the relative orientation of the growth ampule with respect to gravity, ensuing stable or unstable thermal and solutal gradients interact to form complex interacting fluid, thermal, and composition fields. LTT grows on earth under totally mixed conditions. A previous flight growth of LTT in the MEA furnace on STS- 61A in October, 1985 showed a high degree of convection in the melt. Since neither the magnitude nor the direction of the residual gravitational vector were known on that flight, a proper theoretical analysis could not be performed on the data from the experiment. The analysis of this flight sample served as the basis for continued ground based research and the development of the subsequent flight experiment which will be flown on the AADSF in 1996.

While the forthcoming experiment will provide the intermediate quantitative data in a reduced gravitational field, it is only through the utilization of magnetic fields on orbit that a diffusion-

dominated growth is expected to be attained. Recent numerical simulations (part of this program) have shown that a substantial reduction in the magnitude of the residual convection with the consequent diffusion growth conditions as evident from the segregation field, is possible on orbit with even a modest size permanent magnet. Aside from damping the steady flow due to the average gravitational field, the magnetic field on orbit is expected to reduce or eliminate the potentially deleterious effects of the unsteady (g-jitter) component. It is also worth noting that the interaction of the Lorentz force with the double-diffusive convection in the melt on earth and on orbit is in itself an interesting phenomena not studied before.

Interim Results and Future Plans:

Preparatory work has been carried out at both Langley and Marshall and numerical modeling work at Lewis. Langley has grown ground truth samples in its non-magnetic furnaces for two possible growth configurations. The original configuration was to directionally solidify a single long sample, while changing the growth parameters during solidification. An alternative configuration is to use a multiple cell sample with separated smaller LTT cells in series axially. This configuration makes it easier to investigate the effects of different growth parameters, such as a change in residual gravity orientation, magnetic field, or growth rates. The crystals grown are analyzed for both structural perfection and compositional homogeneity. The compositional profile is the most sensitive measure of convection during growth and is measured by a wavelength dispersive electron microprobe.

Two LTT samples have been delivered to date to MSFC for growth in its 5 Tesla magnetic furnace. One LTT sample has been grown in that furnace but due to unrelated operational problems (translation and loss of the cold end heater during the run), a poor quality sample was obtained. The furnace has since been repaired and the second sample is scheduled to be grown. Additional experiments will be carried out in the magnetic furnace at MSFC to optimize the crystal growth and magnetic field parameters. Experimental, sample analysis, and modeling data will be integrated into a final experiment package for a microgravity experiment.

Numerical modeling is well underway at Lewis. It is believed that this is the first modeling effort for a non-dilute alloy combining both thermal and solutal buoyancy-driven convection, and magnetic damping. Recent studies include all relevant experimental parameters and physical phenomena in the melt, together with realistic gravity orientations (both axially and non-axially aligned). Details of the double-diffusive convection and segregation fields in the melt as a function of both gravity level and magnetic field size were also obtained. The resultant radial and axial segregation fields in the solid are also obtained. Interim results show that even average residual acceleration levels of the order of 10^{-5} g significantly affect the segregation phenomena, in agreement with previous flight data. Further work has also shown that a relatively modest magnetic field should be sufficient to achieve an essentially diffusive growth on orbit.

Future plans calls for ground work in a magnetic furnace and continued modelling on predicting and comparing with experimental data for a systematic examination of the phenomena at hand, and for specifying the required magnetic field for microgravity experiments.

Test of Magnetic Damping of Convective Flows in Microgravity

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Other contributor: Terry Rolin, USRA/NASA Marshall Space Flight Center.

Summary as of April 27, 1994 to be distributed at the MSAD microgravity materials science program review, May 24 and 25, 1994.

Objectives

The fundamental objectives of this work are (1) to test experimentally the validity of the modeling predictions applicable to the magnetic damping of convective flows in conductive melts as this applies to the directional solidification of metallic and semiconductor materials in the reduced gravity levels available in low Earth orbit and (2) to assess the effectiveness of magnetic fields in reducing the fluid flows occurring in these materials during space processing that result from density gradients (driven by the residual steady-state acceleration or g-jitter), or surface tension gradients (Marangoni flow). To achieve these fundamental objectives, the following specific objectives are being pursued:

- a) Carry out a comprehensive ground-based program of crystal growth and characterization using a carefully chosen set of materials. Some of these materials have been intensely studied in environments that have not simultaneously included both low gravity and an applied magnetic field. These include a dilute alloy (Ga-doped Ge) in which solutal effects will be negligible and four solid solutions, Ge-Si, InSb-GaSb, Cu-Ni, and Ag-Au, with liquid density ratios of 2.18, 1.07, 1.012, and 0.538, respectively. All five systems will be processed by the Bridgman-Stockbarger method using two diameters. In addition, the Ga-doped Ge and Ge-Si systems will be float-zoned to study the effects of magnetic suppression of Marangoni convection.
- b) Test the validity of magnetohydrodynamic modeling predictions in characterizing the effectiveness of a magnetic field for eliminating convective interference with segregation using applied magnetic fields on Earth and in space,
- c) Characterize as completely as possible any material that will be grown in space to determine the effects of reduced gravity on the heat and mass transfer processes that occur during growth.

Role of Microgravity

Because one objective of this study is to test the validity of magnetohydrodynamic modeling predictions in characterizing the effectiveness of reducing gravity for suppressing convective flows in a modest magnetic field, the requirement for reduced gravity is self-evident. The specific requirement for the space environment is due to (1) the unavailability of an adequate reduced gravity resource except in space and (2) the fundamental reasons for the validity and value of this study. The first point refers to the requirement of hours to days of continuous reduced gravity for these experiments which prevents them from being done in Earth-based low-gravity facilities including sounding rockets. The fundamental reasons for pursuing this work are twofold. First, there is the question of how well we understand the combined effects of reduced gravity and an applied magnetic field on an electrically conductive liquid. Only a series of experiments can answer this question. Second, the application of the combination of reduced gravity and an applied magnetic field to crystal growth of materials with

conductive melts is expected to provide a means, perhaps the only means, of achieving mass diffusion controlled growth in large diameter crystals anywhere on or in orbit about the Earth.

Significant Results and Future Plans

Experimentally, work has been carried out on several material systems including three of the five specifically discussed in the proposal and others that are of interest because they are expected to help determine the optimum parameters for the flight apparatus. Of the three materials systems in the proposal, several ingots of Ga-doped Ge have been grown at zero field and at 5 T. The results to date are puzzling in that complete mixing is observed in the zero-field ingots and nearly the same result is seen in the ingots grown in a 5 T field. Many lines that appear to be interface demarcations were observed in all ingots. The cause of these lines has tentatively been ascribed to either the translation mechanism used to translate the furnace or the temperature control during growth. In either case, we believe we have solved this problem and we are eager to see the results of the first ingot grown in the magnetic field following the improvements to the system. One ingot of $\text{Ge}_{0.95}\text{Si}_{0.05}$ has been grown in the improved system in zero field but has not been analyzed at this time. One ingot of $\text{Cu}_{0.95}\text{Ni}_{0.05}$ has been cast.

Since inception of this program, the attention of the modeling effort has been focused on two fundamental issues. First, the influence of residual gravity parallel to the growth interface in space on convection in the melt, and second, characterization of convective intensity (on Earth, in space, with and without magnetic fields) in pseudo-binary systems characterized by rejection of the more dense material at the growth front. Results indicate that for lightly doped systems the convective intensity in typical semiconductor melts is about 50-100 times more sensitive to gravity parallel to the growth interface than to the normal component of the gravity vector. In the second area, we continue to work on improving the numerical techniques for more accurate and efficient simulation of thermo-solutal convection, and we have focused attention on improving our understanding of convection in systems experiencing stabilizing solutal gradients on Earth. We have shown that convection in these systems is not eliminated by solutal gradients and that a residual convection persists. This residual convection is not benign and results in higher radial compositional variations than would be expected to be present under diffusion-controlled growth. It does not, however, alter the axial concentration profile from the diffusion controlled case.

To broaden the scope of materials and especially to enhance the Marangoni flow part of this investigation, a collaborative agreement has recently been signed by NASA and the Kristallographisches Institut (KI) of the University at Freiburg, Germany. Under the terms of this agreement, several additional materials will be grown in the MSFC magnet including several materials to be grown in the KI mirror furnace using a floating zone technique.

In addition to what is suggested above, the most significant activity planned for the near-term is to begin the determination of the role of *g*-jitter (in Earth's gravity) on the compositional distribution of grown crystals. Ultimately, of course, this investigation was selected for flight definition and flight experimentation is the goal. Before the issuance of the next materials science NRA, the Science Concept Review will be held for this project.

The near-future plans in the modeling area include: (a) investigation of the sensitivity of systems experiencing solutal forces to gravity parallel to the growth surface, (b) continue work on modeling of magnetic and micro-gravity effects on thermo-solutal convection, and (c) detailed simulation of magnetic experiments of Ga:Ge and Ge-Si now in progress.

Crystal Growth of ZnSe and Related Ternary Compound Semiconductors by Physical Vapor Transport

**Principal investigator: Dr. Ching-Hua Su, Staff Scientist
Universities Space Research Association**

Summary

This work was a joint effort including participants from Universities Space Research Association (USRA), NASA Marshall Space Flight Center (MSFC), Marquette University Materials Science and Metallurgy Program, Santa Barbara Research Center and Department of Materials Science and Engineering, State University of New York at Stony Brook. Other contributors included Center for Photonic Materials and Devices, Department of Physics, Fisk University and research associate program of National Research Council (NRC).

The materials to be investigated are ZnSe and related ternary semiconducting alloys (e.g., $\text{ZnS}_x\text{Se}_{1-x}$, $\text{ZnTe}_x\text{Se}_{1-x}$, and $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$). These materials are useful for opto-electronic applications such as high efficiency light emitting diodes and low power threshold and high temperature lasers in the blue-green region of the visible spectrum. The recent demonstration of its optical bistable properties also makes ZnSe a possible candidate material for digital optical computers.

The investigation consists of an extensive ground-based study followed by flight experimentation and involves both experimental and theoretical work. The objectives of the ground-based work are to establish the characteristics of the crystals grown on Earth as a basis for subsequent comparative evaluations of the crystals grown in a low gravity environment and to obtain the experimental data and perform the analyses required to define the optimum parameters for the flight experiments.

The objectives of the proposed investigation are the following:

- a) to determine the relative contributions of gravitationally driven fluid flows to the incorporation of impurities and defects and the deviation from stoichiometry observed in the crystals grown by physical vapor transport due to irregular fluid-flows and growth interface fluctuations.
- b) to evaluate the effect of gravity on the vapor transport process by examining the compositional distribution of the ternary compounds grown in the process.
- c) to assess the relative amount of strain developed during processing at elevated temperatures caused by the gravitational weight of the crystals.
- d) to obtain a limited amount of high quality space-grown materials needed for various property characterization and device fabrication and thus assess the effect of microgravity on the device performance.

The investigation consists of extensive ground-based experimental and theoretical research efforts and concurrent flight experimentation. The objectives of the ground-

based studies are to (i) obtain the experimental data and conduct the analyses required to define the optimum growth parameters for the flight experiments, (ii) perfect various characterization techniques to establish the standard procedure for material characterization and to also quantitatively establish the characteristics of the crystals grown on Earth as a basis for subsequent comparative evaluations of the crystals grown in a low-gravity environment, and (iii) develop theoretical and analytical methods required for such evaluations.

The following are the specific tasks:

a) Establish quantitative correlation between growth parameters (thermal fields, translation rates, vapor species, partial pressures, ampoule geometry, compositions and heat treatments of starting materials, and oriented seeded or unseeded conditions), growth interfaces shapes, compositional redistribution, densities and distributions of dislocations, impurities, small grain boundaries, second phase inclusions, twins, and other structural properties of the crystals grown by physical vapor transport.

b) Evaluate the effectiveness of gravitationally driven convection in the growth process by performing experiments under various vapor transport orientations relative to gravitational direction (i.e., horizontal, vertically stabilized and destabilized configurations).

c) Develop a theoretical model to delineate the effects of mass transport and heat transfer on the distributions of alloy composition, the structural defect (dislocation), the impurities, and the solid-vapor interface shapes during the process of physical vapor transport and compare the results with those obtained in (a) and (b) above and thus establish a fundamental understanding of the crystal growth process.

d) Establish the partial pressure three phase curves of the vapor species in these system by measuring the optical absorption of the vapor phase coexisting with the condensed phases.

e) Evaluate the fundamentals of the current vapor transport theories by performing measurements of the partial pressures of the individual species and the vapor transport rates simultaneously.

f) Perform structural and opto-electronic characterization and thus establish the correlation between the structural, electrical and optical characteristics of the grown crystals and the processing parameters.

g) Evaluate the potential benefits of microgravity processing for device applications by means of fabricating devices from both ground- and space-grown materials.

During the first year of the investigation, the research efforts were concentrated on the binary compound ZnSe. Most of the above tasks were accomplished which include the purification of starting materials of Se by zone refining, the heat treatments of the starting materials to adjust the stoichiometry, the vapor transport rate and the partial pressure measurements of ZnSe, the comparison between the measured mass transport rates and the theoretical results, the unseeded crystal growth of ZnSe and ZnTe by physical vapor transport, and various characterization on the grown ZnSe crystals.

Microgravity Chemical Vapor Deposition

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Objectives

Commercial chemical vapor deposition (CVD) processes currently employ reactors developed through decades of empirical trial and error. There is a need for an improved understanding of the complex physical and chemical processes underlying CVD so that future reactors and processing conditions can be designed and modified much more efficiently and effectively. This research seeks to develop this improved understanding of the processes underlying CVD. An important part of the research effort is to determine key features of meaningful reduced-gravity experiments: features such as maximum acceptable gravitational and vibrational levels, minimum experiment time, critical experimental geometries, and instrumentation requirements.

Background

CVD is an important industrial technique with applications in such diverse fields as semiconductors, optics, and wear- and corrosion-resistance. The nature and quality of the layers formed are dependent on mass and energy transport as well as homogeneous and heterogeneous chemical reactions and nucleation. Scientific understanding of the CVD process is hindered by the difficulty of separating the heat and mass transport due to externally forced convection from that due to the internal processes of buoyant thermal convection, buoyant solutal convection, and thermal (Soret) and solutal diffusion. Complications also arise from the forced convection due to volume changes arising from both reactive chemistry and thermal effects. A better understanding of these effects is essential in order to achieve desired improvements in perfection, uniformity, and size of grown layers and in order to provide an engineering design basis for CVD systems.

Approach

Ground-based experiments and numerical investigations are providing both basic scientific information on the heat and mass transfer effects central to the CVD process and information necessary for defining specific, follow-on reduced-gravity investigations. A horizontal CVD reactor is used for the growth of indium phosphide (InP) by metalorganic chemical vapor deposition (MOCVD) from trimethylindium ($\text{In}(\text{CH}_3)_3$) and phosphine (PH_3) in a hydrogen carrier gas. A replica of the reactor's flow channel is used for laser velocimetry (LV) measurements of the flow fields in this reactor geometry. In the numerical efforts, finite volume techniques are being used to model flow and deposition for the MOCVD of InP and the CVD of silicon. Additional numerical efforts focus on thermophoretic corrections for laser velocimetry data and on optimizing experimental geometries and operating parameters for flight experiments.

Need for Microgravity

Strong buoyant convection, arising from both thermal expansion and solutal inhomogeneities, is a dominant effect in the heat and mass transport of CVD. In many cases, the velocity components due to buoyancy exceed those due to external

forced convection. By conducting experiments in reduced gravity, this strong buoyant convection will be greatly reduced and it will become possible to resolve other important heat and mass transport effects such as coupled thermal-solutal diffusion and deviations from the ideal-gas assumption. This improved understanding of heat and mass transport will result in significant advances in the engineering design of CVD systems.

Significant Results to Date

The research to date has produced results which have enhanced the current understanding of CVD while indicating areas in which further work is needed. The deposition pattern of InP demonstrates the importance of modeling and measuring deposition upstream of the leading edge of the susceptor. The growth pattern in this region indicates the presence of at least two reaction paths for the deposition of InP on the substrate. The shortage of chemical reaction kinetic data for the MOCVD of InP lead to the modeling of Si deposition from silane, a system in which the chemistry is much better understood, as an additional test of the numerical model.

Work performed by this group and others shows that while a vertical cylindrical reactor may at first appear to be highly symmetric, very slight deviations from an axial gravity vector can result in highly non-axisymmetric flows. By contrast, flow in a horizontal rectangular duct is relatively stable with respect to small directional changes in the gravity vector within the vertical symmetry plane.

The modeling effort has clearly demonstrated that using gas mixtures to simulate reduced gravity is inadequate due to thermal diffusion effects. Initial indications are that steady experimental gravitational levels of less than $10^{-3}g$ should be sufficient for meaningful reduced-gravity experiments.

Flow measurement experiments and numerical modeling have shown the importance of careful inlet design for obtaining fully-developed flow without the occurrence of flow-separation or recirculation in the inlet nozzle.

This research effort has demonstrated the importance of full knowledge of the thermal boundary conditions for accurately modeling CVD. Hence, infrared (IR) imaging has been used to provide temperature measurements of three walls of the MOCVD reactor flow channel in hydrogen and nitrogen flows. These measurements have shown that the transport gas and flow field strongly influence the reactor wall temperatures.

Future Work

Future plans for this research effort include refinements of the experimental and numerical studies. Improved InP growth rate data and additional measurements of the thermal boundary conditions for the InP growth will allow more exacting tests of the numerical model.

The parametric flow field study by LV in the replica reactor will be extended to include gas mixtures and depositing flows.

Numerical studies of the gravity vector out of the vertical symmetry plane as well as time-varying gravity vector studies will allow refined definition of critical flight experiment conditions.

METALS AND ALLOYS

CASTING AND SOLIDIFICATION TECHNOLOGY (CAST)

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Summary

The objective of the CAST experiment is to perform a detailed characterization of the effects of convection on the governing growth parameters for unidirectional dendritic solidification. It accomplishes this by combining the results from computational experiments, one- g_e experiments, and microgravity experiments.

The $\text{NH}_4\text{Cl-H}_2\text{O}$ system was used. It is a transparent low melting point metal-model that freezes dendritically. The properties necessary for computational modelling and optical diagnostics are either well known or have been determined by the authors. In addition, the solute (water) is less dense than the solvent (similar to superalloys), making it an interesting material for the study of convective flows.

A numerical fluids thermal model (FTM) was created to predict the evolution of the solutal and thermal fields and the local percent of solid and liquid during the solidification. The code calculates contraction and buoyancy driven flows and is capable of analyzing both one- g_e and microgravity cases. A linear stability model (LSM) was also created to determine stability limits for the transition to convection during solidification. It applies linear stability theory to investigate perturbations to a calculated base state by using extended Darcy conservation equations which also include the effects of solidification shrinkage.

For the ground-based and microgravity experiments, a 28.5 wt% $\text{NH}_4\text{Cl-H}_2\text{O}$ solution was sealed in an optical quality 25 by 16 by 8 mm quartz cuvette. Thermoelectric devices placed at the top and bottom (16mm x 8mm) surfaces provided the initial temperature gradient and mushy zone and controlled the cooling ramp rate to accomplish the directional solidification. The following cooling rates and temperature gradients were used: 4.5, 22.5 and 40°C/hr at 5°C/cm, 9, 45, and 80°C/hr at 10°C/cm, and 13.5, 60 and 67.5°C/hr at 15°C/cm.

The primary data during the flight experiments were holograms. Ground based experiments also used particle tracking, Schlieren and central dark ground method of phase contrast, and Mach-Zehnder interferometry.

The onset and development of convection was characterized and related to the dendritic mushy zone growth. In the early period of solidification, cellular flow initiates in the inverted

(diffusion) layer at the interface, satisfying a Rayleigh number criteria which includes the height of the mushy zone. The growth rate of the mushy zone increases and later, another stage of flow occurs, called pluming, which also satisfies a critical Rayleigh number criteria. The flow now includes fluid from within the mushy zone and again increases the growth rate. The form of each Rayleigh criteria demonstrates that the mushy zone represents a stabilizing influence in the occurrence of flow. Stability analysis using the LSM showed that the additional factor of shrinkage flows opposite to the direction of growth presents a counter-acting effect to the mushy zone influence, decreasing the stability limit for the onset of the flows.

Further into the solidification process, a phenomenon called jetting occurs. Bulk liquid flow rates actually decrease and channels appear within the mushy zone through which high speed flows propagate. Along with the jetting and the changes in flow rate, the interface growth rate slows while the region immediately in the vicinity of the jet grows more rapidly, creating what is called a chimney.

Individual dendritic growth is influenced by the orientation of the fluid flow. Upward flow from the cooler bottom of the cuvette slows the dendrite growth dramatically. In contrast, warmer flow from the upper region of the cuvette which propagates downward, increases the growth of the dendrite. This effect is attributed to the difference in thermal and solutal diffusion rates ($D_T/D_S = 70$) for this system.

Although one- g_e driven fluid flow increases growth rate, the long term effect is still below that of microgravity solidification. Computational predictions show that gravitational driven flow initially increases growth rates above that of microgravity by providing fresh solute to the interface. This effect becomes minimal at $10^{-3} g_e$ and higher. Once steady growth is achieved, the highest gravity level has the lowest growth rate, with the growth rate increasing with decreasing gravity level until $10^{-4} g_e$ is reached. This later reduction in growth rate for the higher gravity levels results from changes in the bulk concentration into which the dendritic front is growing. The flow velocities which influence this mixing are linearly dependant on the gravity level and are on the order of 10^{-2} cm/sec at one- g_e and 10^{-5} cm/sec at $10^{-3} g_e$, approaching the value for zero-gravity.

Measurements of the size and composition of the diffusion layer ahead of the dendritic front show that it grows in size during the early stages of solidification. Under one- g_e , the layer breaks down and significantly reduces in size. In microgravity the layer widths followed an inverse relationship to the cooling rates as would be expected and fall within the theoretical calculated values of $2D/R$, where D is the diffusion coefficient and R is cooling rate divided by temperature gradient. The one- g_e cases do not show such a trend but rather appear to be dictated by either the critical Rayleigh number for breakdown (which limits the height to that below theoretical for the slower cooling rates) or an increased diffusivity effect (which increases the height above theoretical for the faster cooling rates).

Containerless Processing of Oxide Superconductors

NASA Grant #NAG8-832

William H. Hofmeister (PI), Robert J. Bayuzick and R. H. Hopkins (Co.I.'s), James R. Olive (graduate student)

Research Summary

Since the discovery of superconductivity in lanthanide-based perovskite systems, considerable effort has been concentrated on the synthesis and characterization of these materials. The YBaCuO system has received the most intense study, as this material has shown promise for thin film and bulk application. There are problems with the application of bulk materials; weak links, poor connectivity, small coherence length, oxygen content and control, environmental reactivity, phase stability, incongruent melting behavior, grain boundary contamination, brittle behavior, and flux creep. The extent to which these problems are intrinsic or associated with processing is the subject of controversy. This study seeks to understand solidification processing of these materials, and to use this knowledge for alternative processing strategies, which, at the very least, will improve the understanding of bulk material properties and deficiencies.

In general, the phase diagram studies have concentrated on solid state reactions and on the $Y_2Ba_1Cu_1O_x + \text{liquid} \rightarrow YBa_2Cu_3O_{7.5}$ peritectic reaction. Little information is available on the complete melting relations, undercooling, and solidification behavior of these materials. In general, the understanding of undercooling and solidification of high temperature oxide systems lags behind the science of these phenomena in metallic systems. Therefore, ongoing research has been and will be to investigate the fundamental melting relations, undercooling, and solidification behavior of oxide superconductors with an emphasis on improving ground based synthesis of these materials.

Complete understanding of the solidification behavior of copper oxide superconductors necessitates knowledge of the thermophysical properties of the melt. Viscosity, surface tension^[1], heat capacity^[2], as well as nucleation frequency^[3] can best be measured in microgravity. In fact, given the difficulty of processing these materials on earth due to container reactivity, large density differences of components in the melt, and low thermal conductivity, microgravity experiments may be the only means of accurately determining these properties. These parameters are necessary to model phase transitions and melt texturing processes and to evaluate the glass forming ability of these types of melts. In addition, it will be possible to produce benchmark materials in space.

This research project has been funded by NASA Microgravity Science and Applications Division for a three year period. During this time significant progress has been made in understanding the above mentioned phenomena^[4]. The liquidus of the $YBa_2Cu_3O_{7.5}$ has been determined at 1730°C, 200° higher than reported in the literature. In addition, deep undercooling of these materials has been accomplished. In many cases tetragonal $YBa_2Cu_3O_x$ was solidified directly from the melt, demonstrating that formation of Y_2O_3 and $Y_2Ba_1Cu_1O_x$ can be avoided by melt processing and undercooling^[5]. Two new solidification phases have been found in conjunction with tetragonal $YBa_2Cu_3O_x$; a pseudocubic $YBa_2Cu_{3.2}O_x$, and tetragonal $BaCu_2O_x$. These new solidification structures provide an alternate path to subsequent formation of superconducting orthorhombic $YBa_2Cu_3O_{7.5}$. Initial annealing experiments have produced materials with very high intragranular critical current densities.

Further research will continue experiments with $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ using drop tubes at Vanderbilt University, the 105 meter drop tube at the Marshall Space Flight Center, aero-acoustic levitation at Intersonics, Inc., acoustic levitation and microwave heating at JPL, and electrostatic levitation at JPL. Ultra High Speed Thermal Imaging (UHSTI) will be used in conjunction with aero-acoustic levitation to obtain accurate thermal information during cooling and recalescence and to measure solidification velocities. Samples will be examined microstructurally in both the as-processed and annealed conditions, by optical microscopy, scanning electron microscopy, and transmission electron microscopy. Powder X-ray diffraction will be performed at the Marshall Space Flight Center. Differential thermal analysis and high temperature x-ray diffraction will be performed at the High Temperature Materials Laboratory at the Oak Ridge National Laboratory. DC magnetization and associated measurements on selected materials will be performed in collaboration with Ames Laboratory. Annealing schedules will be examined to take advantage of alternative solidification phases as precursors to the formation of the orthorhombic superconducting phase.

One of the primary goals of further research is to extend current ground based studies to include several other compounds both within the YBaCuO system and in other copper oxide superconductor systems. Within the YBaCuO system, at least one other high T_c superconductor has been discovered, the 1:2:4 compound. This new compound as well as several off-stoichiometric composition materials will be processed in order to better understand the phase relationships in this system. In the BiSrCaCuO system, a glass structure can be produced over a very wide range of compositions. Using a new glass-ceramic processing technique developed at Ames Laboratory, amorphous Bi-2212 precursor material has been rapidly crystallized at favorable reaction temperatures under uniaxial load, resulting in a well-textured material with improved superconducting properties^[6]. Current experimental techniques will be used to determine critical cooling rates necessary for glass formation in these and other materials.

An additional objective of this program is to develop collaboration with other groups and provide access to the unique processing strategies developed by the microgravity program. For example, Ames Laboratory is interested in processing $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7+\delta}$ in the Vanderbilt drop tube developed under the existing grant. Ultimately this research effort will lead to a proposed flight experiment where investigators from industry, national laboratories, and universities could participate in highly controlled experiments on the melting and solidification behavior of oxide superconducting systems.

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SUMMARY FOR

COUPLED GROWTH IN HYPERMONOTECTICS

(NAS8-39717 January 28, 1993 - January 27, 1996)

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Objective

The overall intent of this project is to provide an improved fundamental understanding of solidification processes in monotectic alloy systems. The project focuses on the development of aligned fibrous microstructures by controlling the coupled growth process through directional solidification under the proper conditions. The project specifically addresses three main questions. (1) Is it possible to obtain steady state, diffusion controlled growth in a hypermonotectic alloy through microgravity processing? (2) How does growth rate influence the microstructure of monotectic and hypermonotectic alloys processed under diffusion controlled growth conditions? (3) How does alloy composition influence the microstructure of alloys processed under steady state, diffusion controlled growth conditions?

These questions are being addressed through an effort which includes both an experimental segment and a theoretical segment. The theoretical work addresses modeling of the reactions at the growth front starting with the basic differential equations governing the process. Specifics which pertain to the fact that one of the product phases is a liquid will be included in the model.

The experimental segment of the project requires processing samples under conditions which avoid instabilities due to constitutional supercooling and due to convection. This experimentation requires use of a high thermal gradient to growth rate ratio and processing under microgravity conditions.

Necessity of Microgravity Conditions

In most cases it is assumed that microgravity conditions are required for processing hypermonotectic samples in order to avoid sedimentation of the higher density immiscible liquid phase. However, work carried out as a portion of this research has shown that the formation of

the immiscible liquid phase in the liquid ahead of the solidification front can be avoided. The prevention of formation of this liquid requires establishment of steady state growth conditions through use of the proper thermal gradient to growth rate ratio. However, when steady state growth conditions are established, a solute boundary layer forms which makes the sample convectively unstable. This instability and the resulting flow which it causes is sufficient to disrupt the steady state coupled growth process in the alloy. If steady state, diffusion controlled coupled growth conditions are to be established, hypermonotectic alloys must be processed under microgravity conditions in order to minimize convective flow.

Significant Results to Date

There have been several very significant findings that have resulted from this research effort. Perhaps the most dramatic is the establishment of steady state growth conditions in a hypermonotectic transparent metallic analog sample. This sample was processed using a thin (12 μ m) sample cell and a temperature gradient stage microscope. The thin cell and horizontal orientation helped minimize difficulties with convection and permitted establishment of steady state growth conditions. This was the first demonstration of steady state growth in a hypermonotectic sample.

Work has also been carried out utilizing metallic samples in the aluminum indium alloy system. These samples have been processed utilizing NASA's KC-135 aircraft in order to obtain alternating gravity level conditions. During the low-gravity portion of flight convective flows were damped sufficiently to permit coupled growth and the formation of a fibrous microstructure. Longer duration microgravity conditions, such as are obtainable during low-earth orbit, are required for establishment of true steady state growth conditions.

Work is currently underway on the development of a meaningful theoretical model describing coupled growth in monotectic samples. In addition, investigations are underway to determine the most appropriate container material for use with these alloys.

Professor M. C. Flemings
Department of Materials Science and Engineering
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Alloy Undercooling Experiments
NASA Contract NAG8-865

SUMMARY

Objectives :

The Materials Processing Center at Massachusetts Institute of Technology has been actively conducting research on the undercooling of metals and alloy systems in an effort to understand the solidification of undercooled liquids and develop novel routes to process materials with unique microstructures. The technical approach selected involves planning for the upcoming International Microgravity Laboratory (IML-2) shuttle-based experimentation and conducting ground-based solidification research to anchor models on the solidification of undercooled metals and alloys. This program is designed to provide an understanding of how microgravity influences undercooling, to what levels space processing of materials can enhance the ability to achieve greater degrees of undercooling, and what the effect of microgravity has on the ability to demonstrate phase selection and control subsequent microstructural evolution.

Microgravity :

Undercooling in reduced gravity environments has shown promise by producing materials which exhibit improved chemical homogeneity through refinement of the product microstructure and a concomitant reduction in microsegregation. By lowering the power required to position the levitated sample inside the solidification vessel and thus reducing internal convection within the melt, we hope to achieve greater undercoolings in microgravity than are possible on earth. Higher undercoolings should result in a finer dendritic structure and superior properties for near-net shape castings. Selection of metastable solidification structures and phases has the potential to provide additional improvements in material properties. Microgravity is thus an integral requirement for the successful attainment of the goals of this program.

Significant Results and Future Plans :

Ground-based experimentation

Terrestrial experimentation on the undercooling behavior of metals has been facilitated by the use of containerless processing of metal and alloy systems. Samples are electrodynamically levitated, induction heated and then subsequently cooled to produce undercoolings on the order of 25% of the absolute equilibrium liquid freezing temperature. This work has produced rapidly solidified product microstructures characterized by metastable phase morphologies which can be produced using either free levitation or glass encapsulation techniques.

Binary alloy systems involving Ni-Sn, Fe-Ni, Fe-Co, Fe-Cu, and Co-Cu have been investigated as part of this program to define the process of nucleation, growth, and recalescence behavior in undercooled melts. The compositional dependence on undercooling has also been evaluated in order to provide insight into the role of interface kinetics on coarsening, superheating and remelting. The dendrite arm spacing has also been determined, as a function of thermal history, to provide a baseline for comparison to samples processed in a microgravity environment.

The ternary alloy system composed of Fe-Ni-Cr has been investigated as a model system for understanding the undercooling behavior of stainless-steels. The double recalescence phenomenon through metastable bcc phase decomposition can be used to demonstrate phase selection based on processing history. Dendrite growth modeling indicates that although nucleation of the metastable bcc phase is always favored, preferential growth of the stable fcc phase can be attained through manipulation of the heat extraction rate.

Preparations for Flight

We have selected containerless solidification of pure nickel, and of two nickel-tin alloys representing hypoeutectic and eutectic compositions for flight undercooling experiments. The optimal processing conditions have been identified through ground-based modeling and experimentation. In-flight data requirements have been successfully developed and submitted with the experimental protocol for the upcoming STS-65 mission on Columbia utilizing the IML-2 TEMPUS facility. Analysis of both ground-based and microgravity processed samples will continue as part of the post-flight activity in support of the objectives of this program.

GRAVITATIONAL EFFECTS ON THE DEVELOPMENT OF WELD-POOL AND SOLIDIFICATION MICROSTRUCTURES

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Oak Ridge National Laboratory
and
Gary Workman
Johnson Research Center, University of Alabama-Huntsville

The overall goal of this research effort is to achieve a new level of understanding of the effects of both low- and high-g environments on the solidification microstructures and melt-pool morphologies that are produced during fusion-welding and related processes. The research is being carried out through an extension of our recently developed experimental techniques in which large, alloy single crystals are utilized in the study and quantification of solidification microstructures that are produced in both stationary melt pools and in melt pools formed by a moving heat source. Previous investigations of solidification microstructures formed in alloy single crystals have provided detailed microstructural information which cannot be obtained from polycrystalline specimens, and these quantifiable microstructural properties have, in turn, led to the development of new analytical techniques for modeling and predicting solidification-cell structures.

The long-term objective of the present research effort is to carry out both ground-based and KC-135 low-g experiments in order to provide a basis for the development of a series of solidification experiments for future deployment on the Space Shuttle and ultimately on Spacestation Freedom. In addressing this goal, the research effort is directed, in particular, toward increasing our basic understanding of gravitational, surface tension, and natural-convection effects on solidification processes in general and on fusion-welding processes specifically.

The subject research effort has been ongoing for a period of approximately 12 months at this time and is presently proceeding along three well-defined, but related, lines of inquiry.

These lines of inquiry are:

(A) Basic investigations of the solidification microstructures formed in stationary melt pools produced on oriented principal planes of single crystals of the alloy 70Fe-15Ni-15-Cr are being carried out. In order to perform these experiments, large alloy single crystals were first grown by means of the Czochralski technique. These crystals were subsequently oriented, and circular specimens approximately 3.0 mm in thickness were cut from the as-grown boules using electric-arc erosion. In these investigations, circular melt pools have been produced on (100)-, (110)-, and (111)-oriented surfaces by electric arc, laser, and electron-beam melting. The solidification microstructures were then determined using metallographic techniques for both horizontal-surfaces and cross sections. Through controlled sectioning of the samples, it was possible to carry out a three-dimensional reconstruction of the solidification microstructures for the different crystallographic orientations employed. These results represent an established quantitative basis for investigating the effects of both high- and low-g environments on solidification processes in the subject "stainless steel" alloy system.

(B) The austenitic stainless steel single crystals grown as noted above are being applied to the development of techniques for the study of convection-flow patterns in both stationary and transient melt pools. These investigations are proceeding through the addition of a tracer element which is introduced after the melt pool has been formed. After sectioning the specimen, the location of the tracer element can be determined and "mapped" by employing back-scattered electron microscopy. Although these investigations are in a preliminary stage of development, promising results have already been obtained, and it appears that this technique can lead to a better understanding of the physical phenomena associated with mass transport and heat and fluid flow in this practical and important alloy system.

(C) In the course of these investigations, a very interesting phenomenon has recently come to light. This effect consists of the formation of well-defined, oscillatory undulations which appear on the solidified surface as the solidification process takes place. Experiments are presently underway in order to obtain additional information regarding the physical parameters (including gravitational interactions) which control this process.

Evaluation of Microstructural Development in Bulk, Undercooled Alloys

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Summary - NASA Grant NAGW-2844 - April, 1994

It is well established that temperature and compositional density gradients promote macrosegregation during alloy solidification. This problem is minimized in a microgravity environment where, furthermore, the melt does not need to be physically contained. Such an environment could facilitate greater undercoolings and allow processing of high melting temperature or reactive materials while maintaining their purity. Consequently, solidification of a highly undercooled melt could have a uniform and extremely fine microstructure, such as seen in micron-size particles, or other qualities which would enhance material properties. Such consideration might be given to solidification processing of "bulk" or near-net-size castings where the above attributes could be exploited while precluding, for example, powder compaction.

Given that processing in microgravity is expensive, time consuming, and experimentally limited, a definitive series of unit-gravity experiments is necessary, particularly in view of the anticipated solidification dynamics. The intent of this investigation is to develop models and evaluate them by examining microstructural development in undercooled lead -tin alloys with the aim of ascertaining the advantage of processing in a microgravity environment.

To this end, models have been developed which predict microstructural development during eutectic and dendritic solidification of undercooled lead - tin alloys. The eutectic is assumed to grow concentrically from the point of nucleation; for dendritic growth the model assumes nucleation of a single dendrite which grows through the length of the melt. In both cases, upon nucleation of the solid, a rapid rise in the sample temperature from the initial undercooled state to that near the equilibrium one is predicted. This translates into growth velocities which are initially rapid (m/s) but quickly diminish to millimeters per second. Experimentally, nucleation was induced in eutectic (61.9 wt pct Sn) and dendritic (75 and 90 wt pct Sn) lead - tin alloys which

were undercooled from 5 to 25K below their equilibrium freezing temperature. The solidification microstructure was then evaluated for each undercooling from the sample's point of nucleation. For undercoolings from 5 to 20K the eutectic appeared to emanate from the nucleation site in qualitative agreement with the model. Microscopic examination, however, implied the eutectic to extend from the site of nucleation in a spoke-like manner, unlike the continuous sphere of the model. Globular eutectic near the nucleation point and later equiaxed grains precluded a uniform microstructure. With $\Delta T = 25K$, primary lead dendrites were found about the nucleation site which were attributed to the skewed coupled zone. Basically, the actual extent of the expected, and desired, finely aligned eutectic was actually quite small. Experimental results from the dendritic alloys are in agreement with the model, i.e., greater initial undercoolings promote initially finer microstructures. The scale of the microstructure, however, changes rapidly and considerably along the sample length. At undercoolings of 5 and 10K the initially aligned (columnar) structure was interrupted by equiaxed grains. While the results show that a generally aligned solidification microstructure is possible, particularly at higher initial undercoolings, the continually changing scale of the microstructural constituents along the length and breadth of the sample will compromise the desired material properties. No indication of macrosegregation was observed in any of the dendritic alloys. In view of the predictions and experiments, the significance of processing such alloys in a microgravity environment must be carefully evaluated. The results, to date, support processing of high temperature and/or reactive materials, with the possibility of achieving greater undercoolings and a generally aligned structure; achieving fine, uniformly distributed microstructures in "bulk" samples is unlikely.

Work is continuing along several fronts. In view of experimental results, the models are being continually improved and the effect of sample size and geometry on the solidification microstructure continues. Quantitative agreement with the model will be checked through direct observation of solidification. To this end, succinonitrile - 5 wt pct water "alloys," of similar geometry to the Pb-Sn samples, have been undercooled >10K and preferentially nucleated.

NASA Grant No. NAG8-963

Microstructural Development During Directional Solidification of Peritectic Alloys

Summary of Results

Grant Period: July 1, 1993 - June 30, 1996

Principal Investigator: Thomas A. Lograsso

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Microstructural Development during Directional Solidification of Peritectic Alloys

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Objective

Investigation of the peritectic reaction has historically lagged behind its counterpart, the eutectic reaction, even though a large number of industrially important alloys solidify through peritectic reactions. A variety of microstructures can be formed during the controlled solidification of peritectic alloys depending on the growth conditions and level of convection. These microstructures range from two phase dendritic growth to alternating bands of single phase primary and peritectic solids transverse to the growth direction. The type of microstructure which develops depends on the growth conditions typically defined by the ratio of temperature gradient to growth rate. This project focuses on the effect of gravity driven convection on two aspects of microstructural formation in peritectic systems: transitions from primary solid to peritectic solid formation and band formation.

Significant Results

Morphological Transitions - Existing models for peritectic solidification have focused exclusively on the morphology of the primary phase and have not addressed the solidification structure of the peritectic phase, assuming it forms by enveloping the primary phase via the peritectic reaction. However, the peritectic reaction requires diffusion in the solid which is quite slow so that for faster growth rates, the peritectic phase forms directly from the liquid and not through a peritectic reaction. Under this condition, the peritectic phase forms between the primary dendrites or cells and it can exhibit planar, cellular or dendritic morphologies. Theoretical models based on a constitutional supercooling criterion predict the morphology of the primary phase as function of growth conditions and alloy compositions but neglect to consider the relative growth stability of the peritectic solid versus the primary solid. By analogy to the dendrite to eutectic transition, the solid with the higher interface temperature would be the stable solidification product. It is the objective of this portion of the project to examine the applicability of this type of criterion to the phase and morphological selection in peritectic systems.

Our experimental results on the Pb-Bi system have shown that a primary to peritectic solid transition occurs at very low velocities and at very high velocities. The critical conditions obtained for the low velocity transition are equivalent to the constitutional supercooling condition and our results are in agreement with the results of Brody and David. At the low velocity transition, two phase growth of the solid phases at a single isotherm is observed. This two-phase growth occurs under a very specific condition of composition, temperature gradient and growth velocity. Gravitational driven convection in the liquid during solidification leads to extensive macrosegregation and therefore it was not possible to maintain the conditions necessary for two phase growth at

a common interface. By taking advantage of the microgravity environment, it may be possible to minimize macrosegregation effects and sustain two-phase growth conditions.

Future Work

Band Formation - One of the aspects of directional solidification in systems containing a peritectic reaction which is not yet understood on a quantitative basis is a two-phase distribution known as banding. In a banded microstructure, the primary phase and the peritectic phase occur as alternating layers perpendicular to the growth direction. The conditions necessary but not always sufficient for band formation are a hypoperitectic composition (composition within the peritectic isotherm but lower in solute content than the peritectic phase composition) and a planar solid-liquid interface. Several mechanisms for the formation of bands have been proposed but none have been verified experimentally. Convection in the liquid can influence banding, since the nucleation and deposition of phases at the solid-liquid interface is directly affected by changes in the level of solute accumulated in the liquid ahead of the interface. For example, in alloy systems which reject a denser component, banding formation occurs over long length scales (on the order of centimeters) whereas the banding is localized to the transitional region between planar growth of primary solid and planar growth of peritectic solid when the rejected solute is lighter. The objective of this research is to characterize banded microstructures in terms of the changing solid compositions and interface temperatures in a system where convective effects have been minimized in order to develop a quantitative model for band formation.

The In-Sn system was chosen on the basis of two factors: the essentially equal density in the liquid state for the two elements and the low peritectic temperature for a metallic system of approximately 145 °C. If the density of the liquid does not vary with composition and samples are solidified upward, then convection should be as low as possible in ground-based experiments. The relatively low peritectic temperature will allow direct observation and measurement at the solid-liquid interface during directional solidification under controlled growth rate and temperature gradient conditions using experimental apparatus developed for optical analog systems. From these experiments, the sequence of phase deposition relative to the solid-liquid interface can be determined, as well as the variations in interface velocity relative to the imposed rate. If the interface temperature is measured at any point during solidification, then the relative interface positions can be converted to interface temperatures through the known applied temperature gradient. This information will provide the framework for a model describing band formation. In addition, samples with a larger cross-section will be grown in a conventional directional-solidification unit under controlled growth rates and temperature gradients. The composition gradients within individual bands will be determined with an electron microprobe. Interface temperatures and solid phase compositions can be correlated through the phase diagram and used to verify the predictions of the developed model.

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Summary of NASA Sponsored Research Program

Microstructure Formation in Directional Solidification of Binary Alloys Experiment and Computation

NASA Grant: NAG8-962
Principal Investigator: Robert A. Brown
Warren K. Lewis Professor and Head
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Date: April 30, 1994

Summary

The interfacial microstructure formed during directional solidification plays a crucial role in setting the mechanical and electrical properties of metal alloys. Although the basic mechanism for the initiation of interfacial microstructure — morphological instability caused by constitutional supercooling — is well understood, there is currently little predictive understanding of the nonlinear transitions that lead to the interfacial length scales created by solidification conditions beyond those for the onset of the instability. The purpose of this research program is to use ground-based experiments, theory and numerical simulation to establish the mechanism for setting the length scales observed in directional solidification of a binary alloy. The analysis and experiments in this program are based on thin-film directional solidification of transparent, organic binary alloys, such as formed by dilute acetone in succinonitrile. Research to date has emphasized the study of the dynamics of finite-amplitude cellular interfaces that form in this system as the growth rate is increased above a critical value under conditions where convection in the melt has a negligible effect on transport processes. The primary measure of this microstructure is the range of wavelengths of the cells. A fundamental understanding of the mechanisms for microstructure selection is needed for interpretation of future experiments on the solidification of microstructured alloys in a microgravity environment.

The central problem in understanding cellular solidification in two-dimensional systems is the prediction of the wavelengths of cells that exist for a given alloy with specific values of alloy composition, temperature gradient, and growth rate. Linear stability theory predicts a range of growth rates that are unstable for conditions beyond a critical value. The theoretical question is whether a unique value of the cellular wavelength is selected for increasing growth rate, or cells with a range of shapes — and wavelengths — coexist in a large collection of finite-amplitude cells. Previous experiments and some numerical simulations by us suggest that the dynamics of collections of cells leads to a range of spatial wavelengths. Moreover, the dynamics occurs on a very long time scale compared to the time scale for solute diffusion over the length scale (several hundred micrometers) of each cell. The primary goals of this research program are to explore cellular dynamics to the extent of making quantitative the prediction of the qualitative features of the morphology and to develop statistically-based models which can predict the evolution of length-scales during cellular solidification of a binary alloy.

Two accomplishments are needed in experiments and computation to create the data base for constructing a statistical theory: long-time scale experimental data on the statistics of collections of cells and numerical simulations capable of computation of cellular dynamics for large numbers of cells. During the first year of NASA support, we have refined the experimental methods for solidification of succinonitrile-acetone samples in a large-scale thin-film directional solidification system developed by us (C.T. Lee and R.A. Brown, *Physical Review B* 47 4937 (1993)). This system is unique because it allows for long-time (approximately 5000 diffusion time scales)

solidification of well-controlled samples. Experiments this year have focussed on the development of Fourier Transform Infrared Spectroscopy (FTIR) as a analytical measurement of the composition of dilute acetone in succinonitrile samples and the use of the system for precise measurement of the conditions for the onset of morphological instability in the thin-film solidification system. Data from these experiments has been compared with the constitutional supercooling criterion and the stability boundary from the complete linear stability analysis for the onset of morphological instability. The comparison is excellent for the critical value of the growth rate (V_{crit}) for a given alloy concentration (c_0) and temperature gradient (G). However, the structure of the cells seen in the experiments neither resembles the sinusoidal cells predicted by the linear stability analysis nor has a dominant component of the length scale of approximately 500 μm predicted by the linear analysis to be most dangerous. Instead, the length scales of the cells are approximately 100 μm and the cells are irregular. We are in the process of developing a new interfacial imaging system for rapid statistical processing of the cellular structures for quantitative determination of the interfacial morphology.

Theoretical and computational analysis is based on solving continuum transport models for solute and heat transfer coupled with the Gibbs-Thomson condition for interfacial equilibrium. When the temperature field is held fixed, this description is known as the Solutal Model. Several important theoretical discoveries have been made.

- (1) Important theoretical understanding of the long-time-scale dynamics of the cellular interface has come from asymptotic theory and numerical simulation [2]. Here we have demonstrated that the long-time scale dynamics of the interface is caused by the nonlinear coupling between spatially-resonant modes in the cell shape. For example, modes with wavelength λ and $\lambda/2$, interact to cause oscillatory dynamics with a temporal period that scales as the reciprocal of the distance between the present state and a codimension-two bifurcation point between families of cells with these two wavelengths. These conclusions are based on asymptotic analysis valid near codimension-two bifurcation points and are substantiated by fully nonlinear calculations based on solution of the Solutal Model for the interface morphology using a new finite element method. In a large-scale solidification system, this type of nonlinear dynamics is present in abundance and aperiodic, long-scale dynamics is expected, as observed in the experiments. The simulations also have demonstrated another mechanism for interfacial dynamics based on the weakness of the surface free energy of the interface in setting the morphology which leads to highly nonlinear dynamics that is localized in the groove between two neighboring cells [1]; this mechanism causes overshoot in the amplitude of the cells on the time scale for diffusion along the length of the groove.
- (2) The role of convection in effecting the evolution of cellular morphologies from the onset of morphological was investigated by two-dimensional numerical simulations in which thermosolutal convection was added to the Solutal Model described above [3]. The most important finding from these calculations was the difficulty associated with determining the difference between the so-called morphological and convective modes for instability for finite amplitude cells. We have demonstrated that nonlinear states created by both types of instabilities lead to cells separated by very deep grooves for conditions only slightly in excess of those for neutral stability.

Numerical simulations of cellular dynamics that can yield meaningful statistical properties of the interface require the simulation of the dynamics of 10-20 cells simultaneously for long times, an extremely large computation. We have begun the development of a finite element algorithm that will be implemented on parallel computers for performing these simulations. The algorithm will combine the quasi-orthogonal mapping methods developed by us for solution of moving- and free-

boundary value problems, finite-element discretizations and newly developed parallel algorithms for solving large sets of asymmetric, indefinite algebraic equations [4].

List of Publication

1. Tsiveriotis, K. and Brown, R.A., Nonlinear, local dynamics of the melt/crystal interface of a binary alloy in directional solidification. *Physical Review B*, xx, xxx-xxx (1994).
2. Tsiveriotis, K. and Brown, R.A., On the long time scale dynamics observed in directional solidification of a binary alloy. *Physical Review B* xx, xxx-xxx (1994).
3. Mehrabi, R., Öztekin A. and Brown, R.A., Nonlinear analysis of morphological interactions between flow and interface shape in the directional solidification of a binary alloy. *J. Crystal Growth* submitted (1994).
4. Mehrabi, R. and Brown, R.A., Finite-element/Newton method for solution of nonlinear problems in transport processes using domain decomposition and nested dissection on MIMD parallel computers. *Proceedings of the Seventh International Meeting on Domain Decomposition*. American Mathematical Society, in press, 1994.
5. Xia, Y. and Brown, R.A., A test of linear stability theory for the onset of two-dimensional cellular growth of succinonitrile-acetone. *J. Crystal Growth* in preparation (1994).

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SUMMARY

NCC3-290: Transport Phenomena During Equiaxed Solidification of Alloys

PI: C. Beckermann, The University of Iowa

Co-I: H.C. de Groh III, NASA Lewis Research Center

Starting date: Jan. 1993

Period covered by this summary: Jan. 1993 - April 1994

1. Objectives

This study investigates the structural and compositional inhomogeneities resulting from gravity-induced thermosolutal melt convection and solid sedimentation/floatation during equiaxed solidification of metal alloys on a bulk level. Through combined experimental and theoretical work, a numerical simulation model is being developed that allows for the calculation of the individual solid and liquid motions while incorporating the detailed phase interactions on a microscopic scale. The experiments are designed to provide data on the bulk behavior and final segregation and structure of metallic alloys solidifying in an equiaxed fashion, as well as on the transport phenomena occurring on the scale of a single equiaxed crystal growing and moving in an undercooled melt. This data will be used to improve and validate a recently conceived two-phase model of alloy solidification. A unique feature of the model is its intimate coupling of interfacial transport phenomena (e.g., interfacial drag, undercooling) with macroscopic melt convection and solid movement. The work represents a critical step towards the development of a more complete model of gravity-induced transport in alloy solidification and will enable the prediction of the segregation patterns and grain structure on the scale of an equiaxed casting.

2. Relation to Microgravity

The study complements and extends numerous other NASA-sponsored microgravity research programs on solidification of alloys and casting technology. Bulk alloy solidification experiments in a microgravity environment have played a prominent role since the early SPAR and KC-135 flights in the 1970s. The more recent experiments on the space shuttle have concentrated, however, solely on the reduction of melt flow during columnar solidification with a fixed and stationary solid phase. In many castings of technological importance, an equiaxed structure is preferred. Equiaxed solidification is often far from equilibrium (i.e., the melt is undercooled), and the crystals are generally unattached and free to move. In a gravitational field, the density difference between the solid and liquid phases leads to relative motion (e.g., sedimentation), influencing not only the subsequent grain growth, but also causing severe chemical and structural inhomogeneities in the bulk alloy. Presently, no validated model is available to predict segregation and grain size distribution due to two-phase flow in castings. On earth, well controlled equiaxed solidification experiments are difficult to perform because buoyancy-driven melt convection causes uncontrolled grain multiplication due to fragmentation, and the often vigorous melt and solid motions preclude a careful testing of the non-equilibrium solidification model. The microgravity environment, on the other hand, offers the possibility of achieving the equiaxed solidification to occur in a well controlled manner, providing a critical test of nucleation and growth models in the absence of convection and crystal transport. The present ground-based study provides the first predictive model of equiaxed solidification that includes crystal transport in addition to melt convection. The model will be utilized to define and analyze future microgravity experiments aimed at improving present understanding of the role of gravity on the evolution of grain structures and segregation patterns in equiaxed solidification.

3. Progress to Date and Future Plans

3.1 Solidification Experiments

(a) Metal Alloys (NASA LeRC)

The experimental design was finalized and the Bulk Undercooling Furnace was modified to accommodate the added instrumentation. Crucibles were built and successful feasibility experiments were performed using a Pb-15wt% Sn alloy. Additional experiments are planned for the summer of 1994.

(b) Transparent $\text{NH}_4\text{Cl-H}_2\text{O}$ Model Alloy (UI)

Equiaxed solidification experiments were successfully conducted using $\text{NH}_4\text{Cl-H}_2\text{O}$ solutions. The solidification and transport phenomena were visualized and measured using thermocouples, a shadowgraph system, time exposure photographs, and videos. The experiments provide quantitative data on the equiaxed crystal origin, movement, growth, and settling for later comparison with the numerical simulation model.

3.2 Measurements of Interfacial Transport Coefficients

(a) Drag Coefficient of Fabricated Dendrite Models (UC)

The drag coefficient measurements of single equiaxed dendrite models, fabricated from plastic, are completed and the data have been correlated as a function of the settling velocity and several microstructural parameters.

(b) Drag, Heat and Mass Transfer Coefficients of Transparent Model Alloy Dendrites (UI)

The drag coefficient of single equiaxed $\text{NH}_4\text{Cl-H}_2\text{O}$ model alloy crystals has been measured in a specially constructed settling column. The data were also included in the newly developed drag coefficient correlation. In addition, a new correlation has been developed for the multiparticle drag of equiaxed crystals that covers the entire range of solid fractions and grain densities, including previous measurements of the permeability of packed beds of equiaxed crystals. Another settling column was constructed to measure the heat/mass transfer coefficients of settling crystals while they grow in an undercooled melt. Both $\text{NH}_4\text{Cl-H}_2\text{O}$ and succinonitrile-ethanol transparent model alloys are being used in the experiments. Progress was made to develop a suitable correlation framework for use in the simulation model. These experiments will be completed by the end of the second project year.

3.3 Model Studies (UI)

The basic development of the multiphase/multiscale model for equiaxed solidification is complete. Successful validation of the model was achieved for diffusion-dominated purely equiaxed, purely columnar, and mixed equiaxed/columnar dendritic solidification using experimental data available in the literature. The model, including melt convection and solid transport, was implemented on a commercial CFD code and simulation results for equiaxed solidification of an Al-4wt% Cu alloy have been obtained. The next step is to further validate the model using the experimental data obtained under Sections 3.1 (a) and (b). Other parametric studies will be completed by the project end date.

3.4 Publications resulting from this project (11 total) are listed in the accompanying Research Report

SUMMARY

NASA Contract Number NAG8-944 NON-EQUILIBRIUM PHASE TRANSFORMATIONS

Project Director: Kenneth A. Jackson

Co-Investigator: Brian J. J. Zelinski

Near equilibrium, phase transformations depend primarily on the thermodynamics of the system: the redistribution of components caused by the phase transformation are predictable from the appropriate phase diagram. Far from equilibrium, however, the distribution coefficient depends on the growth velocity, so that the equilibrium phase diagram is no longer relevant. The primary objective of this investigation is to explore this phenomenon: to develop an understanding of phase transformations which take place far from equilibrium, and to apply this knowledge to real experimental systems. The principal tool being used is Monte Carlo computer simulations based on the Kossel-Stranski model applied to an alloy, which is equivalent to the Ising spin-1 model. The insights provided by the computer simulations are being used as a guide to study this phenomenon experimentally. Our goal is to develop a quantitative understanding of how the transition from the classical diffusion dominated slow growth regime to the diffusionless rapid growth regime contributes to the segregation and microstructure of real materials. This task is complicated by the fact that phase transitions in this regime are complex, and the presence of non-equilibrium phases and long equilibration times often result in the casual dismissal of results which do not fit neatly into the mold of the classical theory. We suspect that many of these unwelcome phenomena may be explained by the new insights which our modeling is providing.

The modeling predicts that the melting point of an alloy system depends on the diffusion coefficient, so that with slow cooling, near-equilibrium segregation will occur. But our simulations results suggest that on cooling a sample of uniform composition to below the T_0 line, it should freeze quickly and completely, without segregation. Taken above the T_0 line, the sample should melt rapidly to a liquid of uniform composition. It has been reported that titania-coated alumina particles sinter rapidly far below their eutectic temperature. Experimentally, we have explored the surface structure and melting of titania deposited on sapphire, to determine whether the rapid sintering is due to the formation of a liquid above the T_0 line of the alloy. The results so far are ambiguous: there is some evidence of a solidification structure, but the effect could also be due to the presence of a solid phase with very high mobility at low temperatures.

We have been exploring the "the facet effect" experimentally in low-melting organic mixtures. A thin liquid sample on a temperature controlled isothermal stage is being used to study the orientation dependence of the incorporation of dye molecules into an organic crystal. A technique has been developed for seeding the melt in a controlled orientation and a calibration scheme has been developed to relate the apparent color of the sample to the dye concentration in the liquid. Experiments performed in a gravity-free environment will be necessary to eliminate the effects of convection. The rate dependence of the k -value will be explored in experiments performed in the spherulitic growth regime, where this effect should be especially prominent. In this case, the growth rate will be virtually isotropic, but will be varied in time by changing the growth temperature. The common example of this effect is the mineral malachite, which has prominent banding from pale to dark green. An organic dye will be used for this study, and it will be important to elim-

inate unwanted fluctuations in the growth rate due to natural convection. Both of these experimental studies involve an analysis of microsegregation which requires a microgravity environment to minimize the effects of convection. The combination of simulations with experimental studies is viewed as essential not only in providing new insights for the experimental work, but also in keeping the simulations relevant to the real world.

Significant Results to Date

For simulations with no diffusion in either the solid or in the liquid, which is the limiting case for slow diffusion, melting and freezing occur reversibly at the " T_0 " line, where the free energies of the two phases are equal. This is the first direct confirmation of this result. With diffusion in the liquid phase, the k -value depends on both the growth rate and on the diffusion coefficient, in the form $\sqrt{v^2/D}$. For rapid diffusion and slow growth rate, the distribution coefficient approaches the equilibrium value, given by the condition that the chemical potentials of the two components are equal in the two phases. For slow diffusion and rapid growth, the distribution coefficient approaches unity, the value for diffusionless growth. This result provides a new framework for comparison with experimental results in the rapid growth regime. This regime includes splat quenching, laser and electron beam melting, the rapid quenching of small droplets to achieve fine dispersions of uniform composition for subsequent sintering, phase transformations in glass-forming systems, nucleation and the early stages of growth in alloy systems and in multicomponent ceramic or glass systems, etc.

The Monte Carlo simulations reproduce the experimental results on for the growth rate dependence of the k -value in laser melted silicon. The computer results also indicate that the standard rate equations, which work well in describing both alloy systems near equilibrium and also provide the basis of our understanding of crystal growth in single component systems, represent only a limiting case. The overall free energy balance between the solid and liquid phases of the alloy provides the global condition for the equilibrium of the alloy in the diffusionless limit, a result which derives from simulations which depend only on the local jump rates of the atoms. Finally, the simulations have suggested an analytical expression for the growth rate of alloy crystals which should apply generally for phase transformations which occur far from equilibrium.

Future Plans

We have so far explored only a limited range of compositions and alloy systems in the Monte Carlo modeling: we plan to explore a variety of compositions and alloy systems. In some regimes, the dopant atoms are engulfed as liquid atoms, rather than incorporated as crystalline atoms. In some regimes, we see phase separation effects. We have not explored cellular growth in any detail - there should be interesting effects since the k -value depends on the local growth rate. So far, most of our simulations have been done in two dimensions, and we still have many features which will be explored using two dimensional simulations because they run faster. Although we do not anticipate significantly different results in three dimensions, we must do simulations in three dimension sin order to be sure. Our computer code will do three dimensional simulations.

It is clear that there are broad-ranging implications of our simulation results. We plan to pursue the experiments involving the orientation and growth rate dependence of the incorporation of dyes into organic crystals. After the techniques have been worked out in ground-based experiments, detailed experiments in a convection free, 0-g environment will be necessary.

Summary of Project: NASA Grant No. NAG8-905

**METALLIC GLASS RESEARCH IN SPACE:
THERMOPHYSICAL PROPERTIES OF METALLIC GLASSES
AND UNDERCOOLED ALLOYS**

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This project is aimed at studying thermophysical properties of undercooled metallic alloy melts and the relation of these properties to glass formation. Specifically, a method developed here at Caltech to measure the heat capacity and thermal conductivity of an undercooled metallic melt using a non-contact frequency-based calorimetric technique will be used to study samples of $Zr_{76}Ni_{24}$, a Zirconium-based alloy known for its ability to undercool deeply, $Ni_{60}Nb_{40}$, a Nickel-based alloy known as one of the best binary metallic glass-formers, and pure Zr. A complementary experiment will measure these properties for three more Zr-based eutectic alloys. These samples have been incorporated into TEMPUS, the electromagnetic heating and positioning facility onboard the Second International Microgravity Laboratory (IML-2) shuttle flight scheduled for July, 1994.

It is the objective of this project to determine the heat capacity, thermal conductivity and total hemispherical emissivity of these samples. Knowledge of these properties are prerequisite to the development of new processing techniques for metallic glass-forming alloys and will also provide experimental evidence with which to test the various theories of glass-formation and metastability. One method to discriminate among the differing theories of glass-formation is in their predicted behavior for the heat capacity in the undercooled region. This information should also give us insight on the nature of the glass transition and how best to exploit this new class of materials in advanced technological applications.

A microgravity environment is an absolute necessity for this experiment for several reasons. First, liquid metals such as molten $Zr_{76}Ni_{24}$ and $Ni_{60}Nb_{40}$, are extremely reactive. Problems associated with contamination of the melt by any container make taking measurements on "clean" systems difficult. Aside from the difficulties associated with contamination by reaction with the container, the walls themselves also serve as sites for heterogeneous nucleation and limit the amount of undercooling attainable. The measurement of heat capacity of undercooled liquids requires extended periods of time in the undercooled region (on the order of several minutes) with accurate temperature control. Because of these stringent requirements, processing of the samples must be done in a containerless manner. Traditional radio frequency (RF) levitation techniques require so much power to overcome the force of gravity that low temperatures are not easily achievable; in Earth-based laboratories, it is not possible to decouple control of heating and positioning (levitation) powers. For example, the lowest temperature attained during

spectral emissivity measurements done on RF-levitated $\text{Ni}_{60}\text{Nb}_{40}$ (with a melting point of 1184°C) was 1215°C . Although a flowing inert gas environment might make undercooled temperatures accessible to an RF-levitated sample, the AC calorimetric technique requires ultrahigh vacuum conditions (this also rules out other containerless processing techniques such as aero-acoustic levitation). The AC calorimetric technique was specifically designed to take advantage of the ability to decouple positioning power from heating power in microgravity. The undercooled regime is accessible because the power required to position the sample is much smaller than the power used to heat the sample. TEMPUS uses a quadrupole positioner field to hold the sample in the center of a dipole heating field. The baseline temperature resulting from heating by the quadrupole positioner field is $\sim 650^{\circ}\text{C}$, more than 550°C lower than on Earth and below the expected maximum undercooling attainable for the samples.

To date, we have demonstrated the feasibility of this technique by taking measurements on various solid samples in the TEMPUS development module (an exact copy of the flight module), including Nb, W, $\text{Ni}_{60}\text{Nb}_{40}$, $\text{Zr}_{76}\text{Ni}_{24}$, and other Zr-based eutectic alloys. The results agree very well with heat capacities and thermal conductivities for these metals and alloys where measured. We have designed and built the Caltech Total Radiance Bolometer, which will be integrated onto a ground-based levitation system to measure the total hemispherical emissivity of the flight samples and other glass-forming alloys. Knowledge of the total hemispherical emissivity is necessary to obtain an accurate measurement of the heat capacity. In a collaboration with Intersonics Corporation, we have measured spectral emissivities for flight sample compositions over the range of the pyrometers used in TEMPUS (633nm and $\sim 1\text{-}2.5\mu\text{m}$).

Currently, we are in final preparation stages for the upcoming flight. Following the flight, the data will be analyzed and ground-based total hemispherical emissivity measurements will continue. This will, in turn, allow refinement of the noncontact AC calorimetry technique.

PROJECT SUMMARY

PROJECT TITLE: Optical Properties for High Temperature Materials Research

Principal Investigator: Ared Cezairliyan, National Institute of Standards and Technology

Co-Investigator: Shankar Krishnan, Containerless Research, Inc.

1. Project Objectives

The main objective of this project is to obtain definitive values of the normal spectral emissivity of selected high-melting-point metals by two independent techniques, optical pyrometry and laser polarimetry, in order to provide a foundation for reliable radiometric temperature measurements in materials research at high temperatures. Additional objectives are: (i) to establish a database for the emissivity of metals at their melting points in support of existing NASA-sponsored ground- and flight-based experiments, and (ii) to further investigate the wavelength dependence of the emissivity of metals at their melting points.

2. Relevance to Microgravity Research

As an integral part of reliable high-temperature measurements in various materials research in microgravity, accurate data on normal spectral emissivity of materials are needed. Such data are almost nonexistent for high-temperature materials, especially in their liquid phase. The laser polarimetry technique shows great promise in providing emissivity data, however it is essential to validate this technique in terms of well-established pyrometric techniques on materials in their solid phase and/or at their melting points. Therefore, the present work is in support of other microgravity research either by providing accurate emissivity data for the determination of true temperature or by permitting the reliable direct use of the laser polarimetry technique.

3. Background

Normal spectral emissivity measurements by optical pyrometry are performed utilizing a subsecond pulse-heating method developed at the National Institute of Standards and Technology (NIST) [1,2]. This technique allows measurements of not only the normal spectral emissivity, but also heat capacity, electrical resistivity, thermal expansion, hemispherical total emissivity, temperature and energies of solid-solid phase transformations, and melting temperatures [3].

Rapid measurements of the normal spectral emissivity by laser polarimetry have become possible with the recent development of the Division-of-Amplitude photopolarimeter [4,5]. This technique has been applied extensively to levitated liquid materials and to solid materials at room temperature. In this approach, polarized laser light is reflected from the surface and the reflected polarization state is rapidly analyzed to determine the optical properties.

Published results on normal spectral emissivity obtained by laser polarimetry agree reasonably well with those obtained from pulse-heating methods. For Zr, Ti, Nb, Ni, Fe, and Pt, the normal spectral emissivity values obtained at their melting points by optical pyrometry (pulse-heating) and those measured on levitated liquids by laser polarimetry agree to within 5-10%. Some of this variance may be attributed to the differences in the operation of the systems and in the conditions of the specimens.

4. Experimental Methods

Three important steps were needed to realize the experimental objectives. The first was to develop a fast laser polarimeter and its integration with the modified pulse-heating system to enable access to the incoming and reflected laser beams. The second step was to test the entire system by conducting pyrometric and polarimetric measurements to yield normal spectral emissivities of selected solid specimens near and at their melting points. The final step is to extend these measurements to several high melting-point metals with the intent to further

validate the techniques and to generate reliable optical properties data. Detailed description of the principles and operation of the laser polarimeter are given in Ref. 4. The accuracy of pyrometric measurements and operation of the pulse-heating apparatus are described in detail in Ref. 2. A brief summary is given below. Polarized laser light, reflected from the curved surface of the specimen, was analyzed by the four-detector polarimeter. Simultaneously, radiometric data were acquired by two pyrometers that sighted opposite sides of the specimen. In some experiments, one surface of the specimen had a small blackbody hole. Radiometric measurements at this hole yielded true specimen temperatures. A high-speed computer and special a-d converters and triggering hardware enabled high-speed acquisition of the polarimetric and pyrometric signals with millisecond time-resolution.

5. Experimental Results

Preliminary measurements of the normal spectral emissivity have been performed on several metals in their solid phase (Mo, W) and at their melting points (Ni, Fe, Nb). Mo and W specimens were in tubular shape with a blackbody hole in the middle of the length. The pyrometric measurements yielded normal spectral emissivity values independent of other measurements. The pyrometric measurements of the surface radiance were made with a multi-wavelength pyrometer at two wavelengths, 625 and 656 nm, bracketing the wavelength (633 nm) of the laser polarimeter. A second pyrometer operating at 651 nm was used for blackbody measurements. The laser polarimeter provided an independent measurement of the spectral emissivities and optical properties at 633 nm. The results of some of the measurements are summarized below:

- (1) Laser polarimetric results agree to within 1-5% of the pyrometric results (Mo, W).
- (2) Polarimetric measurements on the metals at their melting points show good agreement (1-5%) with the emissivity values derived from the known melting temperature and the (thermal arrest) radiance temperature (Ni, Fe).
- (3) Laser polarimetric data are extremely sensitive to solid-state phase and magnetic transformations (Fe, Ni).
- (4) Laser polarimetry can be used to follow quantitatively, in real-time, the removal of oxide and contaminant layers on the surfaces of the materials.
- (5) Slight specimen instabilities occur during the melting process which limit the duration over which useful laser polarimetric data can be obtained.

6. Current and Future Research

Several shortcomings of the operation of the existing laser polarimeter have been identified. These drawbacks have been addressed in the construction of a new polarimeter which is currently being calibrated and tested at CRI. Because the specimens are cylindrical, the divergence of the reflected laser light is different in the two orthogonal directions. This causes the reflected laser spot to be astigmatic at the field stop. This causes the polarimetric measurements to be quite alignment sensitive. Cylindrical optics will be used to correct this problem. It is anticipated that the new polarimeter will be delivered and tested at NIST later in this year. Further work will also be done at NIST to more accurately characterize the pyrometers and to establish sources of calibration errors. Definitive experiments will be conducted on selected high-melting-point metals. Also the system will be modified to permit laser polarimetric measurements at 900 nm wavelength.

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Containerless Thermophysical and Thermochemical Property Measurements For Liquid Metals and Alloys

Principal Investigator: Robert H. Hauge

Co-Principal Investigator: John L. Margrave

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Objective:

Our research is directed toward obtaining high-temperature thermochemical and thermophysical properties of solid and liquid metals and alloys at very high temperatures. Thermophysical properties of interest are surface tension, density, heat capacity, viscosity, surface optical properties (i.e., emissivity and absorptivity) and thermal conductivity. Thermochemical properties of interest are heterogeneous (gas/surface) reaction rates, rates of formation and loss of refractory thin films and their chemical composition, and rates of formation and loss of gaseous species from the surfaces of very high temperature metal and metal alloy liquids and solids.

Microgravity Requirement:

Property measurements at high temperature in general are best performed without the presence of a container, i.e., in a levitated state. Certain types of measurements require a quiescent state either in the liquid or in the surrounding gas or in both for results to be unambiguously interpreted in terms of fundamental properties such as thermal conductivities and gas/surface reaction rates. This quiescent state in either the liquid or the surrounding gas can only be achieved in a microgravity environment.

Research Summary:

Recent research has focused on the development of accurate, containerless, non-contact methods for measurement of thermophysical properties. Good methods for thermophysical property measurements are considered essential for subsequent thermochemical property measurements. Methods for measuring the thermophysical properties of liquid metals including sample size and density, translational and vibrational modes, surface tension, emissivity and thermodynamic temperature have been developed in our laboratory. Sample shape, size and density are measured with a video-imaging and computer processing technique. The translational and vibrational frequencies are monitored through the use of a continuous duo-lateral position sensor, where appropriate analysis of the data provides surface tension information. A two-channel polarization modulation ellipsometer has been developed to measure the optical constants and emissivity of a levitated metal drop. Preliminary results from the use of these techniques have been promising. Finally, a new type of current concentration levitator has been designed which shows improved sample coupling to the RF power source.

Current Concentrators:

First, a planar current concentration levitator has been designed and tested in our laboratory. The current concentrators as levitators provide improved cylindrical symmetry and improved magnetic coupling to the sample as compared with bare opposed-coil geometries. In addition, the mass and the size of the concentrators allow for more rigid mounting with less sensitivity to vibrations.

Measurements were made where the top and bottom coils are connected such that the RF magnetic fields either add (dipole configuration) or subtract (quadrupole configuration) from each other. It is found that a levitation force exists for both configurations, with the dipole configuration, surprisingly, having a significantly larger levitation force. This indicates that the top and bottom plates act largely as independent dipoles with a large drop in field strength even for small gaps between the plates.

Recently, we have also attached a material with high magnetic permeability to the coil side of both plates and to two sides to provide a return path for the RF magnetic field. The addition of the flux material further enhanced the efficiency of magnetic field.

Sample Shape, Size, and Density Measurements:

A Cohu CCD camera in connection with a 670nm diode laser was used to acquire silhouette image of the samples. Computer software has been developed to provide user-defined pulses for the laser and camera.

A LabView VI reads in a saved video image and scans each line using an intelligent thresholding algorithm. The length and midpoint of each horizontal slice of the sample image is calculated and stored, and, if the image passes a symmetry test based upon analysis of the midpoints of each line, the volume of the sample is calculated from the line length data by an integration approximation given by:

$$V = h \sum_i \frac{1}{4} \pi (n_i l_i)^2 \quad (1)$$

where: n_i is the number of pixels of the i th row, l_i is the horizontal size of each pixel, and h is the vertical size of each pixel.

The sample volume can be used in conjunction with the measured mass of the sample to provide a value for the density of the sample.

Measurements have been obtained during the past year which have proven the validity of the above approach for obtaining submicrosecond video images with resolution determined by the pixel resolution of the camera. One problem which remains is the question of timing the exposure of the video camera such that the sample has circular symmetry along the vertical axis. We are currently developing a real-time symmetry test which will trigger camera exposure only when the sample has the correct symmetry.

Translation, Vibration, and Surface Tension:

The motion and surface tension of levitated liquid metals have been measured with an OT-3210 Duo-Lateral Position Sensing Detector (On-Trak Photonics, Inc.).

Under normal conditions, the sample is at a high enough temperature such that its emitted light is sufficient for direct illumination of the position sensor. A LabView VI was written that reads the seven analog waveforms from the position sensor amplifier into memory for a user-defined length of time at a user-defined sampling rate. The VI then calculates the power series associated with each waveform using a fast-Fourier transform (FFT), then plots and saves on disk the frequency domain spectrum of the data.

All of this information provides us not only with vibrational and translational frequencies, but also allows us to make specific mode assignments.

Emissivity and Sample Temperature:

We have developed a two-channel polarization modulation ellipsometer. In this approach, a photoelastic modulator (PEM-90, Hinds Inc.) is used. A 5mW HeNe laser (632.5nm) has been used as the light source. The incident angle (67.5°) was accurately set by a pentagonal prism. Signals from both detectors were processed through a custom-made lock-in amplifier to obtain $I(1f)$, $I(2f)$ and $I(DC)$, and these signals were sent to our Macintosh for time-averaging and further mathematical manipulation using LabView.

Ellipsometric measurements have been made on liquid copper, gold and platinum. These metals are potentially useful as standards for calibration and testing of containerless measurement techniques.

Future Studies:

With well-developed containerless non-contact thermophysical property measurement capability in hand our focus will increasingly shift to studies of the heterogeneous gas/surface chemistry and reaction rates of metals and metal alloys in the solid and liquid phases. Reliable measurements of reaction rates at moderate and higher pressures will absolutely require the absence of thermally- (density-) induced convection currents at the reacting surfaces. This condition can only be achieved in microgravity. Knowledge of high temperature heterogeneous reaction rates is fundamental to the modeling of combustion processes and the high temperature performance of materials in reactive environments.

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NASA Grant No. NAG8-815 (2/26/90 - 2/25/93)

NAG8-970 (2/26/93 - 2/28/94)

MEASUREMENT OF THE VISCOSITY AND SURFACE TENSION OF UNDERCOOLED MELTS UNDER MICROGRAVITY CONDITIONS AND SUPPORTING MHD CALCULATIONS

The purpose of this investigation is to use the unique attributes of microgravity to determine the surface tension and the viscosity of highly undercooled melts. The project, which combines containerless operation, which makes it possible to process metals with very high melting points, with a microgravity environment has both fundamental and practical justification. The fundamental justification is provided by the fact that understanding the temperature dependence of the viscosity and surface tension of undercooled melts provides important, unique insights into the liquid state and liquid-solid phase transitions.

The practical justification is twofold. Quantitative information on the viscosity and surface tension of undercooled melts is needed for the design of new and better materials processing operations. Perhaps more importantly, the actual techniques used for the experiment, viz electromagnetic levitation have found a broad range of practical uses in the materials processing field. Indeed, it may be shown that the emergence of a whole new field, the electromagnetic processing of materials, is at least in part owed to this particular NASA-supported project. This project will culminate in a Space Shuttle flight scheduled for July, 1994, but even at this stage we can report a great deal in the way of successful accomplishments, including the demonstration of the concept on parabolic flights, extensive publication of the results of ground-based work, the development of methodologies for electromagnetic processing, international interactions, and the development of graduate students and postdoctoral associates.

In the experiment a molten metal droplet (about 10 mm in diameter) is electromagnetically positioned in the TEMPUS electromagnetic processing facility. The droplet is then deformed by electromagnetic "squeezing" forces due to the application of a current pulse through the inner (heating) coils. When the deforming forces are discontinued, the droplet relaxes through a series of damped oscillations, which are recorded on video for post-flight analysis.

It has been shown in classical hydrodynamic theory that the frequency of the oscillations is related to the surface tension, while the decay modulus is related to the viscosity. Thus, through video recording of the oscillating sample and subsequent image processing, we can determine both the viscosity and the surface tension of the

undercooled melt. There are, of course, many other ways of measuring these properties, but for undercooled melts we need to use a containerless technique because the presence of a solid surface would bring about nucleation.

There are two primary reasons why microgravity is necessary to the performance of viscosity measurements on undercooled melts. The very high electromagnetic forces needed to levitate droplets on the ground produces turbulent internal flows which make the measurement of laminar viscosity impossible. Furthermore, the damping of oscillations by electromagnetic forces in ground-based experiments is greater than that by viscous forces, which makes it impossible to observe the viscous damping from which the viscosity measurements are obtained.

Performance of microgravity experiments is also important to verification of the accuracy of measurements of the surface tension of undercooled melts performed in ground-based levitation experiments. There are differences in the surface tension values measured in these ground-based experiments and those measured using other experimental techniques. The differences may be associated with the significant electromagnetic forces present in ground-based levitation experiments, therefore, microgravity experiments are crucial to understanding the effect of magnetic field on surface tension.

From a scientific standpoint the main accomplishments of the research were the development of a methodology and computed results predicting the interaction of an AC electromagnetic field with an axisymmetric metallic body, addressing:

- the electromagnetic force field
- the resultant velocity fields
- sample deformation
- heat generation
- transient response to the changes in conditions

This methodology, in addition to solving the specific problem of designing the NASA-supported microgravity experiment, has played a key role in the emergence of electromagnetic processing as a scientific discipline and has had a major influence on materials processing in general. More specifically, the methodology developed as part of this work has enabled us to describe the operation of induction furnaces, induction stirring, the magnetic damping of convection and many other related phenomena. Over 25 publications have resulted from this work, directly or indirectly, and the PI has received numerous awards in recognition of this effort.

PROJECT SUMMARY

PROJECT TITLE: Containerless Property Measurements of High Temperature Liquids: Emissivity, Temperature, and Thermodynamics
Contract Number: NASW-4687

Principal Investigator: Shankar Krishnan, Containerless Research, Inc., Evanston, IL
Co-Principal Investigator: Paul C. Nordine, Containerless Research, Inc., Evanston, IL

1. Project Objectives

The three main objectives of this project are: (i) to measure the optical properties, including the complex dielectric functions and spectral emissivities of liquid metals and alloys as functions of temperature ($T_m \pm 300$ K), wavelength ($0.22\text{--}1.1\ \mu\text{m}$) and composition using pulsed dye-laser spectroscopic ellipsometry, (ii) to provide spectral emissivity and radiometric data for use in other ground- and flight-based experiments, and (iii) to provide experimental data that will enable advances in theories of the structure-electronic property relationships in liquid metals and alloys.

2. Relevance to Microgravity Research

The relevance that this work has to microgravity research are: (i) this research provides new data and fundamental insights into the optical properties and electronic structure of liquid metals and alloys at elevated temperatures, (ii) this research has provided key spectral emissivity data to the TEMPUS PI's on liquid metals and alloys in the interpretation of ground- and flight-based temperature measurements, and (iii) this research can provide spectral and total hemispherical emissivity data on liquids which would facilitate new ground- and flight-based experimentation to measure other thermophysical property data such as heat capacity and thermal diffusivity and in modelling the radiative energy balance in experiments involving the liquid phase such as crystal growth and directional solidification. Recently, work was conducted to measure the spectral emissivities at $\lambda=633$ nm and radiometric measurements in the infrared on several liquids in support of the TEMPUS experiment scheduled to fly on the IML-2 mission.

3. Background

There are few data on the optical properties of liquid transition metals at elevated temperatures. These properties are of interest in connection with advancing the theories of condensed matter, in improving radiative heat transfer models, determining structure-property relationships that exist in the liquid state, and for thermophysical property measurements. Due to the reactive nature of high temperature liquids, optical property measurements on liquids must be conducted under containerless conditions. A new method of measuring the optical properties of levitated liquids based on laser ellipsometry was originally developed by Krishnan [1] and has since been applied to a large number of liquid materials over a wide temperature and wavelength range.

The present work extended the earlier research to include a fully automated rotating analyzer ellipsometric system coupled with a dye-laser source [2-4]. This has facilitated optical property measurements on liquid metals and alloys over wide temperature ($T_m \pm 300$ K), wavelength ($0.22\text{--}1.1\ \mu\text{m}$) and composition ranges. Measurements of the spectral emissivity as a function of temperature at $\lambda=633$ nm have been made on liquid Ag, Al, Au, Cu, Nb, Ni, Pd, Pt, Si, Ti, Zr, U, Ti-Al alloys, alloys of nickel (Sn, Nb, Zr), and others. More recently, measurements over the entire wavelength range have been made on liquid Al and Zr which show that substantial structure in the optical properties exists in the liquid state. Optical property measurements have also been conducted to study the kinetics of reactions between liquid Zr and gaseous oxygen and nitrogen. Recently normal spectral emissivity values have been obtained for liquid Zr at $\lambda=633$ nm, and spectral emissivity at $\lambda=633$ nm and infrared radiance data have been obtained on liquid Ni, Ni-25% Sn, Ni-32.5% Sn, Ni-40% Nb, and Ni-75% Zr in support of the TEMPUS flight program.

4. Experimental Methods

The experimental methods used in the work derived in large part from established laser ellipsometric measurements of the optical properties of electromagnetically levitated liquid metals [1]. The methods are completely described in the literature [2,4,5] and are summarized below. The experimental arrangement was constructed around an electromagnetic levitator capable of levitating 3-8 mm diameter specimens. In some instances, external heating with the aid of a 300 watt cw CO₂ laser beam was utilized. Convective cooling with high purity helium gas was used to achieve large undercoolings. A pulsed dye-laser was employed as a light source, and an automated rotating analyzer ellipsometer was used to measure the complex dielectric functions and spectral emissivities. Apparent specimen temperatures were measured with an automatic optical pyrometer. In recent experiments on the TEMPUS materials, an infrared pyrometer was also employed. Several laser dyes were used to obtain laser light in the range 0.36-1.0 μm . In addition to the development of the ellipsometer system, some important experimental investigations conducted during the first two years of this work include: (i) optical properties of liquid Al, (ii) optical properties of liquid and solid Zr, and (iii) the emissivities and infrared radiances of materials to be investigated on TEMPUS.

5. Results

Results of the key studies initiated during the first two years of this work have been published in the literature [2-4]. The optical properties of liquid aluminum [2,3] show a remarkable absorption feature at a photon energy of 1.5 eV, very similar to that exhibited by the solid. This feature was not observed for the liquid in previous ellipsometric measurements, in part because all previous investigators employed crucibles to contain their liquid Al specimens. The Ashcroft-Sturm model of parallel-band absorption was used to successfully model the optical properties of the liquid. The derived relaxation time for the absorption was comparable to that for the solid, which is surprising considering that the electrical resistivity of aluminum increases more than two-fold upon melting. A similar result was obtained for liquid Zr [4], where half-widths of absorption peaks approached 0.1 eV to give a relaxation time 1 order of magnitude larger than is calculated from the electrical resistivity of liquid Zr. Liquid Zr exhibits a complex optical property spectrum, with some deviations relative to the polycrystalline solid.

A third key investigation was measurements of the spectral emissivity and infrared radiance properties of liquid metals and alloys that are of interest to PI's on the TEMPUS flight experiment. In these experiments, the spectral emissivity was measured at $\lambda=633$ nm as a function of the apparent specimen temperature at $\lambda=650$ nm, from which true temperatures could be obtained. Concurrently, specimen radiances were also measured in the 1-2.5 μm range with a broad-band infrared pyrometer. Relationships between the true and infrared radiances were derived for liquid Ni, Ni-25% Sn, Ni-32.5% Sn, Ni-40% Nb, and Ni-75% Zr. These relationships will be used by the flight PI's in the interpretation of radiometric results.

Experiments planned for the future include a spectroscopic ellipsometric study of liquid Ni-Zr alloys (the electronic structure of these alloys in the amorphous phase is known) and on liquid Si and Si-based alloys. Some additional work will also be conducted in continuing support of the TEMPUS flight experiments. Structural measurements on levitated liquid aluminum using neutron diffraction have been conducted.

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Effects of Nucleation by Containerless Processing

Grant: NAG8-978

Investigators: Robert J. Bayuzick, William H. Hofmeister, Michael B. Robinson, Craig W. Morton

Summary

A comprehensive investigation on nucleation of the solid from an undercooled liquid is being conducted using pure metals. The critical factors that affect a liquid's ability to undercool to a significant extent before the onset of nucleation are being sought and quantified using classical nucleation theory as a framework for the undercooling results. Three ground based containerless processing techniques are being applied to the effort to obtain sets of undercooling data. These are free fall in the 105 m drop tube at the George C. Marshall Space Flight Center, electromagnetic levitation at Vanderbilt University, and electrostatic levitation at the Jet Propulsion Laboratory. TEMPUS which is an electromagnetic heating and positioning unit will be used in low Earth orbit aboard IML-2 to obtain another set of undercooling data. Each of these techniques for achieving an undercooled melt in a containerless environment has its own unique characteristics in terms of the actual processing of the samples. Therefore, comparisons of the results obtained from each technique will allow a greater insight into the nucleation phenomenon.

Earlier experiments have shown the need for statistical treatment of nucleation experiments in order to achieve a more complete understanding while also eliminating some of the uncertainty in the measurements. A set of data is comprised of over 100 undercooling experiments conducted using the same sample type. The results can then be treated with an approach attributable to Skripov. The work of Skripov has led to the development of a statistical approach which allows the critical free energy of activation and the preexponential terms of the classical nucleation rate equation to be determined for each set of experiments.

The specific differences between the four containerless techniques can be grouped into several main categories which include vacuum level and quiescence. The drop tube and the electrostatic levitator were used to process the samples in vacuum. The drop tube vacuum level was 10^{-6} torr and the electrostatic levitator was 10^{-7} to 10^{-8} torr. TEMPUS will process the samples in vacuum at a level of 10^{-9} torr. The electromagnetic levitator, on the other hand, is backfilled to 1/2 atm of ultra high purity helium after initially evacuating to 10^{-6} torr. Sample cooling is accomplished solely by radiative cooling in the drop tube, electrostatic levitator, and TEMPUS at their respective vacuum levels, whereas, in the electromagnetic levitator, UHP helium is allowed to flow past the sample thereby cooling it by convection and radiation. The second categorical difference is that of sample agitation or quiescence while levitating. In the drop tube, quiescent conditions are present since the sample is in free fall during the cooling and recalescence periods. The electrostatic levitator is not quiescent since a temperature gradient through the sample in the presence of the gravity vector will cause some stirring of the melt. The electromagnetic levitator is also not quiescent since electromagnetic induction produces large internal flows within the melt. TEMPUS, although it is not a completely quiescent technique because of the presence of an electromagnetic positioning force, will have less internal flows than the ground based electromagnetic levitator.

Results indicate fundamental differences in the nucleation behavior of the same sample types in the different ground based processing techniques. For zirconium, which has been processed by all three techniques, the distributions of undercoolings are all non-Gaussian and clustered around the same undercooling but are wider for the electromagnetic levitator and the drop tube than for the

electrostatic levitator. With all three techniques, the distributions retain the same general appearance but shift their centers to higher undercoolings (lower nucleation temperatures) as the material purity is increased from 99.8% to 99.95%. This trend toward higher overall undercoolings but similar distributions was also observed for 99.995% pure zirconium samples processed in the electromagnetic levitator. However, the 99.995% purity material did not undercool as well in the drop tube as it did in the electromagnetic levitator, although the shape of the distribution was similar. For niobium, processing to date has been accomplished only in the drop tube. In this case distributions were much narrower than for zirconium although the percentage undercooling for similar purity levels was approximately the same.

Due to the presence of ultra high purity helium in the electromagnetic levitator, the cooling rate of the samples can be changed by adjusting the flow of cooling gas. Two sets of undercoolings, one obtained at a cooling rate of 100 K/sec and the other at 20 K/sec, have been produced for the same sample type. The shape of the distributions was the same, but the higher cooling rate set of undercoolings was clustered around an undercooling 10 K higher than the center of the lower cooling rate set.

The values of the preexponential factors and the activation energies in the classical nucleation rate equation affect the distributions of undercooling data. A set of undercoolings distributed over a larger range has lower values, whereas a set of undercoolings distributed over a narrower range has higher values associated with it. Thus, for zirconium, the drop tube and electromagnetic levitator had lower associated values than did the electrostatic levitator. The preexponential factors and activation energies tend to be higher as the undercoolings shift to higher overall values. With zirconium, values for the preexponential factors and activation energies ranged from 10^8 to 10^{13} and 13 kT to 24 kT, respectively. For niobium, these values were 10^{34} and 72 kT. Overall, the values obtained for niobium much more closely approach the values predicted for homogeneous nucleation as calculated by Turnbull and Fisher using classical nucleation theory.

The undercooling experiments can be performed using ground based techniques; however, disadvantages with each one in terms of the processing conditions or temperature measurement problems require the use of a microgravity environment to more fully analyze the data. One reason for doing the same experiments in low Earth orbit is to observe the effect of lessening the flows within the melt. In a microgravity environment, positioning of the sample requires much weaker electromagnetic forces; thus, the internal stirring will be decreased. Hence, a comparison of the ground based electromagnetic levitator data to the low Earth orbit data will allow conclusions to be made about the dynamic effects of internal flows on nucleation behavior. Inherent problems in ground based techniques such as error in temperature measurement due to large sample movement or oscillations will also be lessened. The drop tube measurement system is an extreme case because the distance of the sample from the detectors when it nucleates is different from the distance when it has fully recalesced. The measurement error incurred causes the distributions to be wider than they may actually be, thereby causing the observed values for the preexponential factors and activation energies to be low. Experiments in low Earth orbit will allow more accurate distributions of undercoolings to be observed.

Future work includes the shuttle flight experiment and further work with the three ground based techniques. The effects of different cooling rates, vacuum levels, and material purity levels will be further studied.

Summary: Containerless Processing for Controlled Solidification Microstructures

NASA Grant NAGW-2841 (12/91-11/94)

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Objective: The main research objective is the evaluation and analysis of the undercooling and resultant solidification microstructures in containerless processing including drop tube processing and levitation melt processing of selected alloys. The results are intended for use as an experience base for the design of space-based microgravity experiments.

Application to Microgravity Knowledge Base: Containerless processing in ground-based drop tubes may be used to simulate the microgravity conditions via solidification of liquid droplets under free fall conditions. The containerless environment removes a major source of impurities and heterogeneous nucleation sites, allowing for a large melt undercooling. This enhanced liquid undercooling provides the potential for alternate solidification pathways and thus the formation of novel microstructures. By controlling the undercooling level, some level of control of the operative solidification pathway and the resultant microstructure may be realized. The novel structures which may be produced in a ground-based containerless processing facility preview the wide range of possible materials processing experiments which may be conducted in a space-based laboratory. The results of the ground based drop tube study will be used to identify critical experimental variables in microgravity processing, and the analysis may be used to design and predict the science requirements for space experiments.

Research Task Description: The degree of liquid undercooling attainable in a laboratory scale (3m) drop tube and levitation melting system can be altered through the variation of processing parameters such as melt superheat, sample size and gas environment. In a given sample, the competitive nucleation and growth kinetics between equilibrium and metastable phases controls microstructural development. The solidification behavior is evaluated through metallography, thermal analysis and x-ray diffraction examination in conjunction with calorimetric measurements of falling droplets and a heat flow model of the processing conditions to judge the sample thermal history.

Progress to Date: In the current program studies, solidification microstructures are being examined in selected Ni and Mn based systems. The specific alloy selection is based on a metastable phase diagram and solidification kinetics analysis that allows for the identification of unique microstructures and microstructural transitions that may be produced by microgravity containerless processing.

Mn-Al System: Ferromagnetic τ Phase

The MnAl-based alloys represent an important class of ferromagnetic materials which are used in commercial permanent magnet applications. The key ferromagnetic structure is based upon the metastable $L1_0$ τ phase. Prior to our work, the τ phase has only been produced by solid state heat treatments, and hence the magnetic performance has not been optimized by this approach due to a large concentration of defect structures formed during heat treatment. If τ phase could be produced directly from the melt, a significant enhancement of magnetic performance may be expected. Thus, this investigation was initially focused on the experimental study of containerless solidification processing. Our investigation has yielded the first report for a ferromagnetic metastable τ ($L1_0$) phase formed directly from the melt. Complete solidification to τ phase was interrupted by the competitive evolution of an equilibrium ϵ phase during recalescence.

The solidification of a metastable ferromagnetic τ phase in undercooled Mn-Al-C alloys has been examined in terms of the relative thermodynamic phase stability and competitive kinetics. The heat of transformation $\Delta H_f^{\tau \rightarrow \epsilon}$ of the metastable τ phase to the equilibrium hcp ϵ phase and the heat of fusion $\Delta H_f^{\epsilon \rightarrow l}$ of the hcp ϵ phase in a $Mn_{0.55}Al_{0.433}C_{0.017}$ alloy were measured to determine the Gibbs free-energy differences between the metastable and stable phases as a function of temperature. The results indicate that a minimum amount of undercooling 87 K is required to form the metastable ferromagnetic τ phase in a $Mn_{0.55}Al_{0.433}C_{0.017}$ alloy. The attainment of the liquid undercooling required to nucleate the metastable τ phase from the melt may be facilitated by containerless processing. The thermodynamic evaluation was applied further to develop a complete temperature-time-transformation (TTT) diagram of the $Mn_{0.55}Al_{0.433}C_{0.017}$

alloy based on a solid-state transformation kinetics analysis of the $\varepsilon \rightarrow \tau$ reaction during isothermal treatments. This analysis reveals a critical cooling rate of the order of 20 K/s to bypass the metastable τ phase nucleation in agreement with empirical observations and provides a unified guide for the processing of near equiatomic Mn-Al alloys. Based on kinetics analysis the possibility of producing the metastable τ phase in scaled-up sample size (mm size) was investigated. The results provide support for the kinetics analysis and indicate that it is possible to obtain essentially single phase samples of the τ structure in bulk sample sizes, which is compatible with the containerless processing hardware that may be available for space based microgravity experiments.

Ni-V System: Duplex Partitionless Solidification

Solidification processing of eutectic alloys at high rates and large undercoolings has resulted in varying degrees of solute trapping of solid solutions; but as the condition of partitionless solidification approaches, only one of the solid phases typically forms with the same composition as the liquid phase. In contrast to this usual observation, a structure composed of both partitionless fcc and bcc phases has been observed following high undercooling solidification of Ni-V alloys over the composition range 47-51.7 at% V. The Ni-V equilibrium phase diagram features extensive mutual terminal solubilities and an intermetallic σ phase. Containerless processing and rapid solidification suppresses the formation of the σ phase and results in the simultaneous formation of partitionless face-centered cubic (fcc) α and body-centered cubic (bcc) β phases. TEM analysis has identified regions where the α and β grains co-exist in a duplex structure. The observation that two solid phases can form concurrently in a partitionless manner from the liquid phase over a wide (≈ 5 at%) composition range is somewhat unexpected given the strong temperature and compositional dependence of nucleation rates and growth velocities. The presence of this structure appears to have revealed a unique set of kinetic conditions which can allow for duplex solidification. Differential thermal analysis has verified the metastable nature of the duplex supersaturated structure. The duplex partitionless structure exhibited in this system previews an entirely new class of microstructures achievable during high undercooling solidification facilitated by containerless processing.

Current work in the Ni-V system has centered on the kinetic modeling of the solidification reaction. A kinetic model is useful in placing bounds on the values of the relevant experimental parameters under which a duplex partitionless structure can form. The nucleation kinetics model is in good agreement with the experimental results. The analysis has shown that the calculated nucleation temperatures of the fcc and bcc phases are equal at Ni-48 at% V, which is within the range for which the structure is observed experimentally. The growth kinetics model predicts growth velocities that should result in complete solute trapping, also in agreement with experimental results. The nucleation and kinetics models are intended to establish a range of undercoolings and compositions over which a duplex partitionless structure may be expected to develop. These results allow for the construction of a processing map of the reaction, which will be useful in the design and analysis of a space experiment.

Analysis and Modeling of Sample Thermal History and Solidification Kinetics

The availability of thermal history information, such as the level of undercooling, is central to the proper interpretation of a solidification microstructure. To determine the thermal history of a droplet in containerless drop tube processing, direct thermal measurement of a falling droplet was conducted using a calorimetric method. With a given level of superheat, the heat content of a droplet has been determined at the time of impact with the calorimeter by means of a simple heat balance. The method has been successfully implemented with pure nickel and nickel alloys.

As a further aid to solidification analysis, droplet microstructures were used as a guide to understand sample thermal history. The relationship between microstructural scale and level of undercooling achieved illustrates the importance of microstructure as an *in situ* probe for quantitative evaluation of material properties. The concept of an *in situ* probe has particular significance to containerless processing in space in that the effect of disturbances such as external positioning fields on solidification behavior may be analyzed in a systematic way. The experimental determination of undercooling level through non-contact temperature measurement in the investigation will provide a test of the solidification and heat flow models which were developed in order to provide insight into the mechanisms of solidification microstructure development. Moreover, this ground-based experience will also be of value in the design of the science requirements and hardware for a space experiment.

The Gravitational Role in Liquid Phase Sintering

**An Experimental and Theoretical Study of
Macrostructural and Microstructural Changes Induced by Gravity
in Tungsten Heavy Alloys**

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Summary

On July 8, 1994, the International Microgravity Laboratory - 2 is scheduled for flight aboard the orbiter *Columbia*. One set of experiments on that flight will examine the liquid phase sintering of various tungsten heavy alloys under microgravity conditions. Sintering will take place in three cartridges that will be processed in a large isothermal furnace provided by the Japanese space agency NASDA. The data obtained from these experiments will provide insight into the effects of gravity on both macrostructural and microstructural development, including viscous flow shape distortion, grain coarsening, grain coalescence, grain settling, solid-liquid separation, and pore evolution in liquid phase sintering. Experiments identical to those planned for the shuttle flight have been carried out under normal gravitational conditions using a prototype of the flight furnace. This presentation reports on the results of the completed microstructural analysis of the ground-based samples and the progress in understanding gravitational effects on sintering.

Liquid phase sintering (LPS) is a technique used to fabricate many high performance materials ranging from cutting tools to self-lubricating bearings. Generally, LPS involves heating mixed particles to produce a liquid. Densification results from the high diffusion rates in the liquid phase and the capillary forces created by the wetting liquid. New microstructures and insights into the role of gravity will be possible from the analysis of the microgravity samples. Digestion and analysis of these data will lead to revised models. Much of the preliminaries (based on completed ground-based experiments) are in place to expedite these measurements. As a consequence, improved concepts of microstructure coarsening during LPS have been advanced that accurately predict the grain size distribution and the effects of the key process parameters. Most unique is the prediction of the grain growth rate constant variation with the liquid volume fraction. Prior models failed to include the high solids contents where grain contact and coalescence are factors. Alternatively, experiments have been impossible with samples with the separated solid grain structure assumed in existing models. Thus, there is a well recognized gap between theory and experiment. The current research on gravitational effects during liquid phase sintering extends far beyond the concern of tungsten heavy alloys and are applicable to ferrous powder metallurgy, ceramic sintering, covalent high temperature ceramics (SiC and Si_3N_4), cemented carbides, and even solders.

In spite of extensive industrial use of LPS, there are several recognized problems. One is solid-liquid separation due to gravity. Like sand settling in water, differences in densities give segregation of the solid grains. In compositions with an excess of liquid, this leads to a segregated layer of approximately 60 vol.% solid, independent of the actual system solid content. A consequence of settling is that only compositions with an excess of solid (typically over 60 vol.%) can be fabricated on Earth by LPS. Furthermore, the evolution of the final microstructure is poorly understood. We have observed a role of the solid-liquid density difference in the microstructure of the settled region. With small density differences there is slow settling, allowing considerable grain coalescence in the liquid prior to settling. The resulting grain agglomeration leads to a lower solid density in the settled region with a lower grain growth rate. The classic theories of Ostwald ripening do not apply to the high volume fractions of solid needed for Earth processing, because of the solid-liquid segregation. Further complications exist since the theories assume nonzero dihedral angles, spherical grain shapes, and no solid contact. Thus, coarsening theory is not applicable to the high solid contents used in LPS. Additionally, the role of solution-precipitation versus grain coalescence is untested by critical experiments. One point of concern is whether particle contacts induced by gravity contribute to enhanced grain coarsening through coalescence. Alternatively, gravity may impede grain rotation to low energy misorientations, and thereby retard coalescence. Since the microstructure controls the properties, it is important to learn if benefits are possible through altered processing cycles such as under microgravity conditions. The research to date has substantiated significant gravity effects including grain settling, solid-liquid separation, differential grain coarsening, compact distortion, and mechanical property variations.

Clearly, in performing fundamental studies on liquid phase sintering there are several intrinsic problems. Perhaps the most difficult barrier is the phenomenon of solid-liquid segregation due to gravity. The larger the density difference between the solid and liquid phases, the faster the segregation will occur. In the tungsten-nickel-iron system, gravitational settling is particularly pronounced since the liquid has a density of approximately 10 g/cc, while solid tungsten has a density of 19.3 g/cc. For this reason, W-Ni-Fe alloys were selected for this study.

The forthcoming IML-2 microgravity experiments will examine time and solids content variables in parallel with replica experiments performed under ground-base conditions. The three times at 1500°C will be 1, 15, and 120 min. Five presintered alloy compositions ranging from 78 to 98 wt.% tungsten will be used, with a 7:3 weight ratio of Ni:Fe. Two additional alloys will be used at 93 wt.% tungsten, one in the pressed powder (green) state and the other already subjected to 1 min of liquid phase sintering under normal gravitational conditions. This field of compositions, pretreatments, and times will define the gravitational role in LPS. Future experiments will build on this base by considering longer sintering times, higher sintering temperatures, and lower solid contents. Although there is great theoretical interest in dilute alloys with high liquid contents, experiments with low solids contents can not be conducted on Earth without significant solid-liquid segregation. The success of the planned flight on IML-2 will build the needed base to understand the relation to microgravity sintering. Then, future study can expand on this understanding and provide microstructures not obtainable on earth. This will allow critical examination of new theories on the microstructure evolution for LPS materials in general.

Coarsening in Solid-Liquid Mixtures

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1 Summary

The late-stages a first-order phase transformation process are usually characterized by the growth of second-phase domains with low interfacial curvature at the expense of domains with high interfacial curvature. This process, also known as Ostwald ripening or coarsening, occurs in a wide variety of two-phase mixtures ranging from multiphase solids to multiphase liquids, and has a significant impact on the high temperature stability of many technologically important materials. Unfortunately, an understanding of the dynamics of ripening processes is not in hand. Many of the recent theories for the effects of a finite volume fraction of coarsening phase on the kinetics of Ostwald ripening have proposed divergent expressions for the dependence of the coarsening rate of the system on the volume fraction of coarsening phase. As there are virtually no experimental data of sufficient quality to differentiate between these theories, or even provide qualitative information on the coarsening dynamics of low volume fraction systems, the controversy over the dependence of the coarsening rate of the system on the volume fraction remains unresolved.

Previous NASA sponsored work clearly showed that solid-liquid mixtures consisting of Sn-rich particles in a Pb-Sn eutectic liquid are ideal, and perhaps unique, systems in which to explore the dynamics of the Ostwald ripening process. The high coarsening rate in these systems permit accurate kinetic data to be obtained, and the thermophysical parameters necessary to make a comparison between theory and experiment are known. However, in a terrestrial environment experiments can be performed only at the relatively high volume fractions of solid where the presence of a solid skeletal structure prevents large-scale particle sedimentation. In these high volume fraction experiments, a comparison between theory and experiment shows that the solid-liquid mixtures are coarsening faster than predicted by an approximate theory for purely diffusional controlled Ostwald ripening. Thus, the microgravity experiment under development will serve two primary purposes: it will allow experiments to be performed which can be directly compared to heretofore untested theories for coarsening in systems with low volume fractions of solid, and it will eliminate conclusively convection of the liquid matrix and small-scale particle motion within the skeletal structure

as possible sources for the disagreement observed between theory and experiment in the high volume fraction experiments.

A second objective of the spaceflight experiment is to elucidate the reasons behind the formation of a solid skeletal structure during coarsening. In a terrestrial gravitational field there is a critical volume fraction at which this skeleton forms. Our previous work has shown that the level of the gravitational acceleration plays a crucial role in setting the critical volume fraction for the formation of the skeletal structure. However, the mechanisms responsible for the formation of these surprisingly stable percolated solid-liquid mixtures are still very much unknown. The spaceflight experiment will enable us to examine the crucial role one parameter, namely gravity, plays in the formation of these solid skeletal structures.

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An electrochemical method to measure diffusivity in liquid metals

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SUMMARY

This study concerns the use of coulometric titration methods to obtain benchmark values of oxygen diffusivity in liquid metals. The availability of these benchmark values will be useful for many reasons, including, assessing the reliability of different experimental designs and operational procedures for measuring diffusivity on earth, defining the appropriate constitutive behavior of 'Fickian Diffusion' in liquid metals and interpreting the results of flow visualization measurements which use oxygen as a tracer. In other words there are two reasons to measure diffusion coefficients.

First, the accurate measurement of molecular diffusivity in high melting point liquid metals and alloys is of interest from a fundamental view point, largely because molecular diffusivity is an important physical property. For the same reason, the behavior of molecular diffusivity with temperature can only throw more light on the constitutive behavior of the binary system. Second, the 'strength' of low level convection in the microgravity processing of liquid metals in enclosures can be measured by it's effect on the mass transfer of a tracer such as oxygen. For this, it is necessary to know accurately the molecular diffusivity of the tracer in the liquid metal and compare it to the effective diffusivity.

In the last 25 years, coulometric titration procedures have been used to determine values of the diffusivity of elements in liquid metals. The electrochemical cells use highly conductive solid state electrolytes that, under potentiostatic or galvanostatic operation, can establish a known boundary condition at the melt electrolyte interface and, under open circuit operation, can sense the conducting species concentration. Current results by us indicate that convection driven by thermal or solutal gradients is present in most ground based experiments. Diffusivity measurements by necessity involve concentration gradients, and if these gradients are not collinear with the gravitational field, will certainly cause fluid convection that adversely affect the diffusivity measurements. Since mass diffusivities are small in value, concentration boundary layers tend to be formed near solute source/sink locations and this only enhances the solute gradients. Thus even small changes from collinearity are expected to cause considerable convective flow. Indeed, even if the concentration gradients are parallel to the gravity vector, we have conditional stability. Now, diffusivity measurements in most liquid metals are conducted at high temperatures. Therefore, there is also a potential problem of introducing thermal gradients which are not collinear to the gravity vector. Consequently, we have more than one reason that could cause convection on earth. *This makes low gravity necessary to conduct accurate measurements.* Diffusivity measurements using solid state electrolytes have been performed in a variety of geometries by examining either the steady or transient response of an electrochemical cell to constant flux or constant concentration boundary conditions. Data possess considerable scatter, with significant discrepancies between various workers.

Another science objective of this study is to establish a clearer picture of the constitutive

behavior of 'Fickian diffusion' of oxygen in liquid metals. In particular, we are interested in accurately measuring the temperature dependence of the oxygen diffusion coefficient. From such a relationship, we can determine whether the diffusivity dependence is of the classical Arrhenius nature or not. Arrhenius behavior implies a certain mechanism for diffusion. If an Arrhenius behavior is not observed, then clearly a different phenomenon is present that is characteristic of liquid metals. We have some experiments that indicate the behavior is of a non-Arrhenius type and yet these results could have been affected by adverse convective effects. More definitive studies will be done within the present project period.

The need for a low gravity environment:

1) Convection changes the measured diffusivities substantially and we have shown this fact, based on some of our present preliminary ground-based results. Thus we must try and eliminate gravity driven convection.

2) It is difficult to eliminate imperfections such as small temperature gradients and tilts with respect to gravity. Temperature gradients cause radially induced convective flows and a tilt will cause concentration gradients to be misaligned with gravity also generating convection. A low gravity environment will diminish the effect of these imperfections considerably.

3) Low gravity will allow us to obtain our results in more than one way and thus we can verify our measurements by using alternative means such as radial transfer of oxygen. This configuration could not have produced meaningful results in '1-g' because the gradients would not be parallel to the gravity vector and convection would then be instantaneous.

The objectives of the first phase of this study are:

1) To use different container or 'cell' sizes to study the effect of the magnitude of convection on diffusivity measurements. If convection is negligibly weak, then, results with different geometries should give comparably close results. These experiments will use different liquid metals and involve oxygen depletion at different boundaries.

2) To measure diffusivity at various temperature levels and obtain the relationship of diffusivity with temperature.

3) To calculate the effect of natural convection under earth's gravity due to imperfections such as small tilts with respect to gravity. This should be done in order to estimate the role played by imperfections, in limiting the accuracy of diffusivity measurements under 1-g.

In this report we will report some of our present results on the presence of solutal and thermal convection during diffusivity measurements in Sn.

The main result obtained thus far in the study may be summarized as follows:

The measured values of diffusivity depended on the cell size and experimental configuration. Measurements taken in configurations that gave rise to gravity driven convective flows also gave larger values of diffusion coefficients than measurements taken in configurations where the convective flows were apparently weaker. A detailed numerical model with a sophisticated 3-D code was developed, which predicts the effects of imperfections such as tilts and

radial heat losses. Based on this modeling, we conclude that even slight imperfections affect the diffusivity measurements for all of the cell configurations studied. Other observations that were influenced by the cell configurations were made. For example taller cells, which were associated with large time constants, increased the measurement error because of mass transfer through an overflow port. This port was included in the design in order to accommodate the expansion of tin upon heating. Thus, the initial oxygen concentration and cell dimensions both influenced the hydrostatic stability of the tin sample during a transient diffusion experiment. This is not surprising as the transport process is essentially the transient version of the Rayleigh-Bénard problem and the aspect ratio and Rayleigh number are two parameters which are found to define the stability criterion in that problem.

In brief, we believe that gravity driven convection in the melt prevents accurate measurement of the mass diffusivity of oxygen in metal systems by coulometric titration. This situation represents a clear example where a reduced gravity environment is necessary to obtain meaningful values of this important physical property. We intend to perform more experiments and will use the results of these measurements to design a flight based experiment. This will ultimately give a benchmark about which to judge the reliability of ground-based cell designs. In addition, we will measure the temperature dependence of the oxygen diffusivity to clarify the appropriate constitutive equation. All of our experimental studies are currently modeled by a 3-D numerical code that we have successfully developed for convection in closed containers. Future modifications of the code will incorporate 'g-jitter' or residual forces that are expected in a low gravity environment.

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**National Aeronautics and Space Administration
Microgravity Science and Applications Division
Microgravity Materials Science Program**

Summary of Research Activity

Frans Spaepen, Principal Investigator

David Turnbull, Co-Investigator

Michael J. Aziz, Co-Investigator

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Present contract: : Crystal Nucleation, Hydrostatic Tension and
Diffusion in Metal and Semiconductor Melts (NAGW 2838)

1. Objectives of the Investigation:

To develop basic understanding of the phenomena and processes that are central to the microgravity program: crystal nucleation, glass formation and diffusion in the liquid state.

Specific research includes: crystal nucleation studies in elemental metal, semiconductor or quasicrystal-forming droplets coated with different fluxes, droplets with clean surfaces in vacuum, and droplets solidified in a drop tube; dilatometric study of the effect of hydrostatic stress on the nucleation kinetics; experimental and theoretical study of the crystal-melt interfacial tension; theory of multicomponent nucleation and nucleation transients; measurements of the diffusivity in the liquid state from the broadening of impurity profiles after pulsed laser melting.

2. Relation to Microgravity Research:

The research serves the program in three ways.

(i) By developing the basic understanding of the phenomena and processes that are central in the microgravity program, such as crystal nucleation, glass formation, and diffusion in the liquid state. Design of microgravity experiments and analysis of the results requires progressive development of their fundamental understanding.

(ii) By identifying possible experiments for some of the unique ground-based facilities provided by the program. For example, the drop tower, levitation and ultra-high vacuum facilities can be useful for crystal nucleation experiments.

(iii) By evaluating potential alternatives to, or identifying possible limitations of microgravity or containerless experiments. For example, in research under a previous contract we demonstrated in simple drop tube experiments that surface oxide is the nucleant for crystallization of a metallic glass forming melt, and that the use of an appropriate flux can sometimes eliminate the need for containerless processing in undercooling studies. Further exploration of the use of fluxes is part of the present proposal. The use of pulsed laser melting of ion-implanted metals is being evaluated as an alternative method for measuring liquid diffusivities.

3. Significant Results and Plans

1. *Fundamentals of nucleation.* David T. Wu has made important new contributions to the theory of nucleation. They include (i) A more accurate continuum approximation for nucleation theory based on a new approach involving spectral density functions. (ii) An exact solution of the time lag in transient nucleation for both the simple monomer approximation and the more complicated multipath kinetics. It also resolved the controversy over the "prefactor" in previous approximate time-lags. (iii) A general approach to barrier crossing in multicomponent nucleation. The analysis is reformulated to include all paths of nucleation. Starting with simple measurement theory, he defines a global nucleation rate that corresponds to what is observable experimentally. This rate can be calculated at steady state and estimated for arbitrary times, provided the rate matrix and the free energy obey certain constraints. When applied to the special case of a quadratic barrier, the global nucleation rate is *smaller* than the standard result based on the rate of saddle-point nucleation.

2. *Undercooling of melts that crystallize into polytetrahedral structures.* Andrew.V. Wagner has rebuilt the 3m pyrex drop tube, which was used in experiments on glass formation under earlier contracts, so it can be used for solidification experiments on Ga-Mg-Zn droplets. This system is a known quasicrystal former. The aim is to investigate the degree of undercooling this melt can sustain, given that its interfacial tension with polytetrahedral phases such as the quasicrystal, the quasicrystal approximants, and Frank-Kasper phases (such as the MgZn_2 Laves phase) may be quite low. A large number of different sizes have been solidified. A detailed study of their microstructure is underway, including phase identification and quantitative characterization of the phase morphology. The ease of nucleation of the MgZn_2 phase, which we had observed in earlier work on undercooling of Al-Mg-Zn by different techniques, has been confirmed in this system.

3. *Study of the crystal-melt interface.* Frans Spaepen has developed a theory for the temperature dependence of the solid-liquid interfacial tension and its link to the structure of the interface. It was used to reanalyze Turnbull's data on the homogeneous nucleation of Hg crystals from the melt. This analysis showed that the origin of the interfacial tension is a substantial drop in the entropy of liquid due to localization near the crystal; the enthalpy change is small.

4. *The diffusivity of liquid metals.* Michael.J. Aziz measured the diffusivities of Fe and Cu in liquid Al were measured by melting thin Al films with a nanosecond-duration pulsed laser. The thin film geometry eliminated convection in the melt during the experiment and simplified the measurement of the diffusion coefficient in liquid. The transition conductance and the optical reflectance of the Al layer during melting were measured to obtain the melt duration. The diffusivity of Fe was found to be much smaller than that of Cu, consistent with Turnbull's proposal of cluster formation in Fe-Al melts as an explanation of their volumetric behavior.

5. *The undercooling of semiconductor melts* Yan Shao is performing undercooling experiments of silicon droplets in various oxide and halogen fluxes. Many oxide fluxes are reduced by silicon, and as a result lose their effectiveness. Chloride and fluoride fluxes may be more successful for the removal of nucleants. Currently high silica chlorosilicate and fluorosilicate liquids and glasses are being investigated. In a parallel series of experiments, melting and resolidification of uncoated silicon and germanium on different substrates are being investigated with the aim of developing a systematic understanding of the effects of heterogeneous nucleants. Specific substrates include: amorphous and crystalline silica, mica and silicon (for germanium).

Temperature Dependence of Diffusivities in Liquid Metals

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Objectives and Tasks

Due to the complex structure of liquids and, thus, the lack of realistic structure models, our theoretical understanding of diffusion in liquids and its temperature dependence is very limited. Molten metals possess relatively simple structures and, hence, often serve as model systems for liquids. In order to provide guidance in the development of fundamental diffusion theory, accurate self-diffusivity data for molten metals over a wide temperature range are needed.

The tasks to be pursued under this program include the

- development of an efficient technique for dynamic in-situ measurements of the temperature dependence of diffusivities in liquids;
- development of a flight-certified hardware package to perform such diffusivity measurements automatically;
- application of this technique to liquid metals on Earth and under low-gravity conditions;
- establishment of a definitive database for the temperature dependence of diffusivities of liquid metals, to further the development of the theory of diffusion in liquids; and
- exploration of the possibility to simulate low gravity diffusion conditions on Earth in conducting liquids through the application of magnetic fields.

Microgravity Aspects

Over the wide temperature range required to unambiguously determine temperature dependencies of properties, on Earth, convective contributions to mass transport are practically unavoidable. As a consequence, the standard deviations of currently available diffusivity data for liquid metals range from several 10% to 100%. Under low-gravity conditions, this experimental uncertainty can be reduced to a few percent, as has been demonstrated in earlier high-temperature diffusion experiments on the Space Shuttle.

Experiment concept

An initially solid, cylindrical sample has a radioactive isotope electroplated to one end. After melting, radiation escaping through small bores in an isothermal liner/radiation shield is monitored *via* a chain of radiation detectors. The evolution of the signal distribution in the liquid is recorded over a wide range in sample temperature. Utilizing a novel algorithm, the temperature dependence of diffusivity is obtained with high accuracy from the data acquired in a single run.

Work and Results to Date

- Development of a novel algorithm for the evaluation of diffusive concentration profiles without use of the boundary conditions and specialized initial conditions.
- Experiment sensitivity analysis to maximize the distinguishability between various functional dependencies of diffusivity on temperature, and to minimize the radioactive dose and power requirements.
- Design and manufacture of an isothermal diffusion oven, with minimal power consumption, adequate radioactive shielding and ready sample exchange.
- Selection, acquisition, and testing of detectors and data acquisition electronics at elevated temperatures.
- Selection of the radioactive isotopes (according to half-lives and photon energies) to be used in self- and inter-diffusion experiments with tin, cadmium, indium, selenium, tellurium and lead.

COMPARISON OF THE STRUCTURE AND SEGREGATION IN DENDRITIC ALLOYS SOLIDIFIED IN TERRESTRIAL AND LOW-GRAVITY ENVIRONMENTS

NASA Grant NAG3-1446

by

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Summary

The objective is to directionally solidify dendritic alloys in a microgravity environment. The thermosolutal convection in a terrestrial experiment is so extensive that it is impossible to study diffusive controlled growth of dendritic arrays. In microgravity, however, thermosolutal convection would be suppressed, thereby making it possible to solidify alloys with only shrinkage induced convection. Therefore, by carrying out both terrestrial and microgravity experiments, we can compare the structure and segregation in dendritic alloys solidified in both environments and study the roles of both purely diffusional transports and thermosolutal convection on macrosegregation and microsegregation, and on the metrics of the dendritic microstructure.

In the present grant, we are carrying out terrestrial directional solidification experiments and computer simulations of the thermosolutal convection and macrosegregation. We are studying dendritic growth, as it occurs in directionally solidified castings, in which the solid forms as an array of dendrites rather than as an isolated dendrite.

In our terrestrial experiments, 7 mm diameter samples of hypoeutectic Pb-Sn alloys, with compositions ranging from 10 to 58 wt. % Sn, have been directionally solidified at rates of 4 to 66 $\mu\text{m s}^{-1}$ in thermal gradients of 67 to 110 K cm^{-1} . This results in macrosegregation along the length of the directionally solidified alloys and, in some cases, macrosegregation-defects known as freckles. With no thermosolutal convection, the tin content along the length would have been uniform, except for an initial length of the order of mushy zone length. We also observed that the extent of macrosegregation increases with increasing tin content, becomes maximum at 33.3 wt. % Sn, and decreases with further increase in the tin content.

With no convection and by using growth conditions with a small gradient of constitutional supercooling, it is possible to develop solutal build up at the dendrite tips, with the mass transfer at the tips controlled by diffusional transports. In terrestrial experiments, however, the thermosolutal convection in the melt column and the upper part of the mushy zone dominates the diffusional transports. The two effects, diffusional transports and thermosolutal convection, can only be isolated by comparing the segregation and dendritic microstructures obtained in the terrestrial and microgravity grown specimens. Attempts to

suppress the convection by solidifying samples in magnetic fields have failed; thus a microgravity environment is required to successfully carry out such research.

We have prepared many experimental DS castings in which the macrosegregation has been measured. In addition, microstructures have been taken from quenched castings, including regions near the leading part of the advancing mushy zone. With these microstructures, we have discerned that the extent of macrosegregation increases with decreasing growth speed, as the solid changes from a dendritic to cellular morphology.

The intensity of the segregation along the length of the samples can be explained in terms of a parameter, defined as $\lambda_1^2 f_E (C_E - C_t)$, where λ_1 is the primary arm spacing, f_E is the volume fraction interdendritic eutectic, and C_E and C_t are the eutectic and tip compositions in the liquid, respectively. Alloy composition, thermal gradient and solidification rate control the variables λ_1 , f_E and C_t . Although this parameter has been helpful in categorizing our experimental results, a better theoretical base requires numerical simulations of the thermosolutal convection.

Numerical simulations have been done using the thermal conditions and composition of one of the experimental castings exhibiting freckles. The simulation shows upward flow next to the walls of the container, reminiscent of plumes that emanate upward from a remelted channel within a mushy zone that ultimately becomes a freckle. The segregation is extensive; starting with a melt of 23.2 % Sn, the concentration of solute in the channels is as much as 31.5% Sn and Sn-rich liquid leaves the mushy zone for the all-liquid zone by the upward flowing plumes. With no convection, the simulation shows essentially no macrosegregation, except for an initial transient length associated with the thermal dynamics of a developing mushy zone.

Our present grant has provided convincing evidence that thermosolutal convection is primarily responsible for detrimental forms of macrosegregation in directionally solidified castings. In the microgravity environment, the thermosolutal convection would be greatly diminished and convection would be confined only to the flow of interdendritic liquid required to satisfy solidification shrinkage. During the last six months of the grant, we plan to define the growth conditions for microgravity experiments that could be done in an existing NASA furnace for a space flight experiment. We will run numerical simulations and study the effects of sample diameter, thermal gradient, solidification rate, and alloy composition.

Particle Engulfment and Pushing by Solidifying Interfaces

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One of the main issue in the fabrication of particulate metal matrix composites by melt processing techniques is that of uniform distribution of particles in the solid matrix. The distribution of reinforcing particles depends on the interaction between various composite phases in three different stages of processing, that is during transfer of particles from gas to liquid, during particle-particle interaction in the liquid, and during transfer of particles from liquid to solid. All these interactions are influenced by gravitational acceleration. A uniform distribution of particles in the matrix cannot be achieved without the control of particle behavior at the liquid/solid (L/S) interface during solidification. Understanding the particle/interface interaction is of great fundamental as well as practical importance.

When a moving solidification front intercepts an insoluble particle, it can either *push* it or *engulf* it. In the case of engulfment the solid grows around the particle. If the solidification interface becomes unstable resulting in formation of dendrites or equiaxed grains, two or more solidification fronts can converge on the particle. Even if the particle is not engulfed by one of the fronts, it will be eventually *entrapped* in the solid at the end of the local solidification.

Several theoretical models have been proposed. They can be broadly classified as thermodynamic models, thermal properties criterion models, and kinetics models. The last are more complete and by far more complicated.

All the kinetic models developed to date are based on the concept of a critical interface velocity (V_{cr}), below which particles are pushed and above which particles are engulfed. The existence of V_{cr} has been demonstrated experimentally on a number of systems, including metallic systems. Computer curve fitting analysis of experimental results showed that the critical velocity depends on particle radius (r) according to the equation $V_{cr} = a/r^n$ where a is a constant and the exponent n ranges from 0.28 to 0.9.

Experimental work and theoretical analyses by many investigators have demonstrated that a number of factors influence the engulfment/pushing transition. They include: solidification velocity (V), interface surface energy (γ_s), viscosity of liquid (η), fraction of particles (f), particle size (r), thermal conductivity ($\mu = K_p/K_L$), temperature gradient at the interface (G), interface morphology, and convection level in the liquid (solutal, thermal, buoyancy driven).

The scientific objectives of this research are to enhance the fundamental understanding of dynamics of insoluble particles at L/S interfaces, to quantify the role of natural convection on particle behavior at the L/S interface, and to improve the general understanding of physics associated with solidification of liquid metals - ceramic particles mixtures.

The need for conducting experiments in micro-gravity (μ -g) results from the experimental requirements and the limitations of ground-based testing. The basic experimental requirements include a convection-free environment, and limited flotation or sedimentation of particles. However, natural convection occurring during ground-based experimentation causes particulate agglomeration and alters the thermal and solutal

field, and thus the critical velocity. For negligible convection experiments (*e.g.*, by using capillary size crucibles) curvature effects and rolling friction between the container and the particles may significantly alter the results. In addition, particles flotation or sedimentation is unavoidable.

Some of the investigators of this research have previously developed an analytical model for evaluation of the critical velocity in which energy transport was used only for calculation of interface shape. The equilibrium velocity was then obtained on the basis of force balance. Under NASA sponsorship the analytical model has been further developed. The critical velocity was evaluated by coupling both the force and thermal fields. Typical calculations are shown in Fig. 1. A numerical model to include diffusive and convective mass transport is under development.

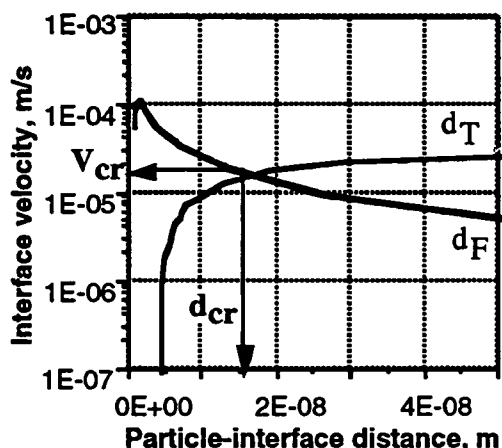


Fig. 1 Evaluation of critical velocity for a 4 μm radius SiC particle in succinonitrile.

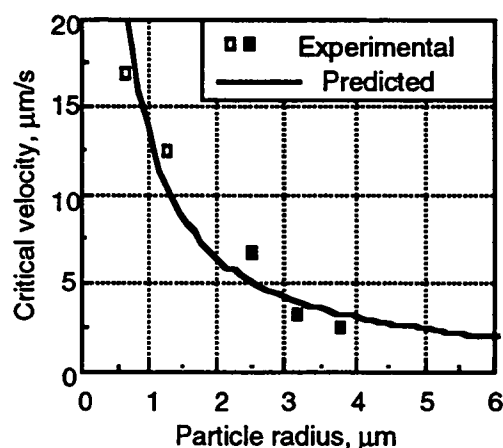


Fig. 2 Correlation between the critical velocity and particle radius in pure SCN ($G_L=108 \text{ K/cm}$).

Experimental work was conducted with transparent organic materials (succinonitrile + water) and polystyrene particles (0.5 to 7.5 μm radius) to validate model prediction. Typical experimental and calculated results are shown in Fig. 2. Future experimental work under this program will include ground experiments to provide information to further develop the analytical and numerical models for particle pushing/engulfment, to identify the optimum systems and variables for flight experimentation, and to produce preliminary validation of the existing models. Additional goals of ground experimentation include generation of the data base for comparison with $\mu\text{-g}$ experiments, and preparation of samples for flight experimentation. Micro-gravity experiments will also be conducted to evaluate the critical velocity during convection-free solidification, to produce definitive validation of the model, and to generate indirect information on interface surface energy.

FOAM METALLIC GLASS

(NASA Grant No. NAG8-947)

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A new idea and a new processing approach to achieve as-cast bulk amorphous materials in the form of foam metallic glass are investigated. By sudden decompression of a melt that is seeded with a volatile liquid, the dispersed "foaming" or blowing liquid vaporizes, taking its latent heat of vaporization from the melt, thereby adiabatically and homogeneously cooling the melt. Due to a high decompression rate, a sufficient cooling rate may be produced to yield a foam that may have an amorphous structure. The objective of this research is to determine the conditions for which such foamed metallic glass formation is possible, to identify the optimum processing parameters, and to develop a process to produce a technologically applicable material.

The initial experiments are designed and performed in a 1-g environment. Should the ground-based studies prove positive, then the next step is to take advantage of the microgravity environment for optimizing the metallic glass processing. It is essential that there be a uniform dispersion of small drops of the blowing liquid in the melt. These two liquids greatly differ in density and will tend to separate quickly at 1-g. Microgravity will eliminate this separation. In addition, decompression to a relatively large evacuated and cooled chamber will maximize the chances of achieving cooling rates approaching one million degrees per second which is the quench rate for which metallic glass formation may be possible. The environment of space provides an ideal large vacuum chamber.

Ground-based studies are currently in progress. The materials foaming principle was initially studied using a modified commercial PARR Pressure Cell with p-terphenyl (an organic) as a sample material. The foaming conditions of p-terphenyl were identified by systematically changing process parameters such as the mixing-ratio of water to p-terphenyl, stirring speed, cell gas pressure and release temperature. The explosive process by sudden pressure decompression of melted p-terphenyl in which water is dispersed, produced an interconnected foam rather than separated pieces or particles. High water to p-terphenyl ratio and high releasing pressure helped to produce foam with high porosity or low density. Foam density as low as 12 % of the original density of p-terphenyl has been obtained. Materials characterization elucidated foam open porous structure.

Limited experiments of foam processing of metal tin, using the same apparatus for p-terphenyl and water as the foaming agent, were performed. Although in some surface areas, holes and convex hills and dimples were observed, no massive foam was produced. Design of a more sophisticated apparatus is currently in progress in order to disperse water uniformly into tin to improve the chances of producing foam tin. The new apparatus will use a high power ultrasonic horn to emulsify and disperse foaming liquid, and a cooling media purging system to cool and protect samples.

Eventually an easy metallic glass former such as $\text{Au}_{55}\text{Pb}_{22.5}\text{Sb}_{22.5}$ will be processed. Theoretical and numerical analysis of the dynamic foaming process will complement the experimental program. Materials characterization, and mechanical and electrical testing will be conducted on the samples to reveal the structure and properties of foamed materials and to provide insight for adjusting processing parameters to improve the possibilities of producing a foam metallic glass. Materials characterization will typically include x-ray diffraction, optical microscopy, scanning electron microscopy, analytical electron microscopy and calorimetric analysis. After the initial processing of tin and of Au-Pb-Sb, the foaming of other metallic materials will be explored.